UNIVERSITY OF EDINBURGH

Investigations on Configuration in the Carbohydrate Group by means of Conductivity Measurements in Boric Acid Solution.

Thesis presented by
Herbert Taylor Macpherson B.Sc.,
candidate to qualify for the degree of Ph.D.

May 1937

CONTENTS.

Part One

I N T R O D U C T I O N

Since the time of Biot, who in 1835 observed that boric acid increased the rotatory power of tartaric acid, it has been known that some interaction takes place when solutions of certain hydroxy-compounds are added to solutions of orthoboric acid, H_3BO_3.

The most evident of these changes is the increased acidity of the boric acid solution. Thus in 1878 Klein[1] found that if a neutral concentrated solution of mannitol is added to a solution of boric acid so dilute as to have no action on blue litmus, then the resulting solution immediately turns the litmus red: the reaction, indicative of a marked increase of acidity, is very delicate and requires only a very small concentration of boric acid. The literature contains numerous papers on the effect of sugars and related alcohols on the acidity of boric acid and borate solutions: the following are typical:-

Berenschtein and Ajzenberg[2] found that fructose had practically the same effect as mannitol in increasing the dissociation of boric acid solutions. The effect was greatest when there were 2 molecules of fructose to 1 molecule of boric acid present in the solution, and it increased with the concentration. Sucrose had no action: maltose, lactose, glucose, erythritol and galactose affected the dissociation in

increasing order. All of these, however, had an effect considerably smaller than that of fructose.

Thomas and Kalman[3] discovered that equivalent amounts of neutral solutions of glucose, galactose, mannose and arabinose develop the same acidity when added to a solution of sodium borate. Xylose and fructose exert the greatest effect, pH 4 being reached, while rhamnose is the least effective. The effect falls to zero when the initial acidity of the borate solution is increased to pH 3.

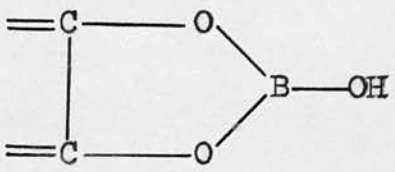
Voicu & Axente[4] state that the hydrogen-ion concentrations of solutions of boric acid are increased when sucrose is added. The change takes place immediately and there is no further slow variation. A similar effect is observed with glucose and fructose, the magnitude of the change increasing with increasing concentration of the boric acid. With sucrose, the change in hydrogen-ion concentration is at a maximum in the presence of 1.03% boric acid and is inappreciable at a concentration of 4.13%. The authors consider it probable that sucrose forms a compound with orthoboric acid (H_3BO_3), but not with the tetraboric acid ($H_6B_4O_9$) present in more concentrated solutions.

This increase in acidity of solutions of boric acid on the addition of certain substances has been put to practical use in the titrimetric estimation of boric acid[5]. Boric acid is normally only feebly ionised in aqueous solution and cannot be estimated in the usual way, namely by titration with alkali in the presence of phenolphthalein. The addition of a few drops of alkali produces a pink colour indicative of the end-point, when in reality only a small part of the boric acid has been neutralised. If now a little glycerol or mannitol is added, this pink colour immediately disappears and more alkali may be added until the solution again turns pink: a little of the glycerol or mannitol is added each time the pink colour reappears. At the true end-point, the further addition of glycerol or mannitol will not affect the pink colour. A much sharper colour change is noted at the end-point proper than at the "pseudo" end-points caused by incomplete dissociation of the boric acid. In this way boric acid behaves as a fairly strong monobasic acid, and can be accurately estimated in solution.

Berenstein[6] used various sugars in place of glycerol and mannitol, and in each case estimated the amount of boric acid which was indicated by the final

end-point. He found that with boric acid alone in aqueous solution, the end-point with alkali and phenolphthalein corresponded to only 10% of the boric acid present. If glucose or lactose were added to the boric acid solution, then the end-point showed 25%, with galactose 40%, but with fructose, as with glycerol and mannitol, 100%.

It is to be noted that in most of the work on the acidity and dissociation of boric acid, efforts are being made to find a quantitative relationship between the relative amounts of hydroxy-compound and boric acid producing the maximum effect on the dissociation of the boric acid solutions. It is obvious for example, that some reaction is taking place when mannitol is added to boric acid solution, and the investigations were carried out for the most part on the assumption that the changes which the boric acid undergoes were due to the combination of the two substances to give ethereal salts of the form first proposed by van't Hoff[7]



To test this compound formation theory,

Magnanini[8] undertook a series of conductivity experiments: he began by determining the conductivities of solutions of boric acid containing various amounts of mannitol. He found the conductivity of boric acid to be enormously increased by the addition of mannitol, the increase becoming greater, up to a point, with increasing addition of mannitol. "One must therefore assume", he states, "that since mannitol itself is a non-conductor some electrolyte is formed in the solution";application of the Guldberg-Waage theory of Mass Action led him to the conclusion that a compound of boric acid and mannitol was formed in the solution, the substances being present in the molecular ratio of three to one. Similar experiments were carried out by Ageno and Valla[9], but according to their conclusions, the ratio is one to one. Magnanini also examined dulcitol in the same way as mannitol and found that it too greatly increased the conductivity of boric acid, but in this case he could find no simple molecular relationship and assumed that more than one compound was formed in solution. He next investigated solutions of tartaric and boric acids: again his results led him to the conclusion that these two acids form at least one compound with one another. This conclusion was subsequently borne out to some extent by the work of Lowry on borotartaric acid: this will be discussed

more fully later.

Magnanini then proceeded to investigate the effect of a large number of organic acids on the electrical conductivity of boric acid solutions. From his results he arrived at the following general conclusions:-

1. The addition of an aqueous solution of an organic acid, containing no alcoholic hydroxyl group, to a solution of boric acid, never augments the conductivity.

2. An increase in conductivity is always obtained when there is an alcoholic or phenolic hydroxyl group in the α - or o-position to the carboxyl group.

3. If the hydroxyl group is not so placed there is no rise in conductivity.

These three laws gave, according to Magnanini, a method for solving the constitution of a number of organic acids soluble in water. Many of these acids, however, are practically insoluble in water and it became of importance to know whether an alcoholic solution of the acid obeyed the same laws. Magnanini used aqueous solutions of the acids containing from 18 to 73% alcohol and found that the same results were obtained as with aqueous solutions. He confirmed these conclusions in his paper of 1893[8] and found that the rule regarding the proximity of the

hydroxyl and carboxyl groups held with open- or with closed-chain compounds: it also appeared to hold independently of the other groups in the molecule, and again it held whether the hydroxyl group was attached to a primary, secondary or tertiary carbon atom. In general, no augmentation of conductivity was observed with acids containing the hydroxyl groups in any position other than the α - or o-position.

The work of Böeseken and his co-workers at Delft during the past twenty-five years has revealed that this property of increasing the conductivity of boric acid solutions is more generally shared by a large number of polyhydroxy compounds.

Among the first substances which Böeseken[10] examined were the dihydroxybenzenes: "of these", he states, "the o-derivatives are very liable to give rise to new ring systems such as phthalic anhydride, compounds of several benzene rings etc.: this is because the hydroxyl groups are fixed in the same plane as the unsaturated ring. With the m- and p-derivatives no such 5- or 6-atom ring formation is possible, because, since the groups are in the same plane as the ring, the intermediate vertices of the ring prove an insurmountable obstacle. This is no longer the case with the hydrated derivatives of benzene,

since the groups linked to the atoms of the ring are no longer compelled to remain in the same plane as the ring". He points out "the impossibility of preparing lactones of m- and p-hydroxybenzoic acids: similarly the anhydride of hydroquinone is unknown, while quinic acid, which is a m-hydroxy cyclic saturated acid, and also hexahydro-hydroquinone, can both easily lose a molecule of water". In this research Böeseken found that only the o-dihydroxybenzenes form, with boric acid, compounds whose conductivities are great with respect to the sum of the conductivities of the components.

It is to be noted that Böeseken here assumes increase in conductivity to be due to compound formation between the hydroxy-compound and the boric acid, using the van't Hoff formulation[7]. In the course of his later work he gradually accumulates evidence in support of this view. Böeseken extended the conductivity work of Magnanini to glycol, glycerol, pentaerythritol, phenol, catechol, resorcinol, pyrogallol, hydroquinone etc.: he found an increase in conductivity of boric acid in the presence of glycerol, pentaerythritol, catechol and pyrogallol. The other alcohols and phenols caused no increase in the conductivity, sometimes even bringing about a decrease.

Like Magnanini, Böeseken drew some general conclusions from his researches:-

1. When the influence of catechol is compared with the indifference of glycol, it is obviously not sufficient that two hydroxyl groups should be α- or o- to one another; a second condition must be fulfilled.

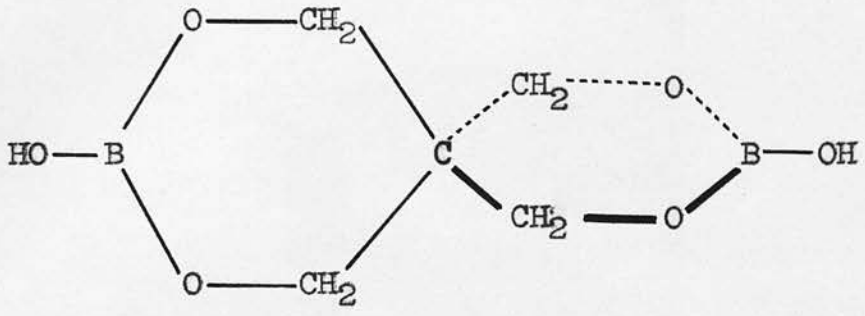
2. The hydroxyl groups must be in a favourable position for the formation of a ring compound with boric acid.

3. The position will be favourable when the hydroxyl groups are cis- to one another and in the same plane as the carbon atoms to which they are attached: since a pentatomic ring is flat[11], this latter condition will obviously be necessary if a ring-compound is to be formed without strain. In certain cases we may get increase in conductivity with the hydroxyl groups in the β-position.

In catechol and pyrogallol the position will be very favourable and a new pentatomic ring can easily be formed: with resorcinol the position is unfavourable. In the simple open-chain glycols, the mutual repulsions of the hydroxyl groups will place them as far as possible from one another on account of the mobility of the saturated molecule; but as the number of hydroxyl groups increases, they cannot place

themselves as unfavourably as in the simple glycols.

Penta-erythritol gives a big increase in conductivity because of the possibility of formation of two hexatomic rings thus:-



Now, if one of the CH_2OH groups of penta-erythritol is replaced by an indifferent atom or group, it is probable that the action on boric acid will be diminished, though it may possibly be still greater than that of glycerol. Accordingly Böeseken[12] examined nitrotricarbinolmethane $CNO_2(CH_2OH)_3$: this substance did actually have a much less pronounced action on boric acid, though it had a much greater influence than glycerol.

The so-called "Boric Acid Test" is based on these conclusions of Böeseken: this test is used chiefly to distinguish between cis- and trans-forms of polyhydroxy substances. If the substance causes an increase in the conductivity of boric acid solution then it is the cis-form, if a decrease, it is the trans-form.

Several other methods are available for determining the actual configuration at carbon atom 1:

1. Cis-compounds have a smaller molecular refraction than the corresponding trans-compounds.

2. Only acetohalogenoses with cis-configuration, will react with trimethylamine to give a quaternary base[13].

3. Trans-glucosides are in general more quickly hydrolysed than the cis-forms[14].

4. The anhydride is more easily formed when the hydroxyl groups are in the cis-position.

5. Optical calculations according to the method of Freudenberg[15].

All these methods have to be used with care, and in the examination of one particular substance, the conclusion reached from one method does not always agree with that reached by one of the other methods. Thus, for example, α-d-mannose is cis- according to method 1 and by the boric acid test[16], whilst methods 2 and 5 indicate it to be the trans-form.

The conductivity work of Böeseken was to some extent borne out by the researches of Irvine and Steele[17]: these investigators studied the action of mannitol and methylated mannitols on the electrical conductivity of boric acid solutions. They found, as

did Böeseken, a very great increase in conductivity when mannitol was added: the substitution of five of the hydroxyl groups by methoxyl groups, leaving only the hydroxyl on number 1: carbon atom unsubstituted, completely removed this positive effect and a small depression of conductivity was obtained. Irvine's results may be summarised as follows:-

Solution	Exaltation of Conductivity
(a) M/2 mannitol	$+ 613 \times 10^{-6}$*
(b) M/2 pentamethyl mannitol	− 19
(c) M/4 5:6-dimethyl mannitol	+ 343
(d) M/2 3:4:5:6-tetramethyl mannitol	+ 565
(e) M/2 2:3:5:6-tetramethyl mannitol	− 20

(b) shows that one hydroxyl group is not sufficient to cause an increase in conductivity: (d) and (e) show that two groups are sufficient, but that they must be cis- to one another: (d) also shows that the effect of mannitol on boric acid is due chiefly to the hydroxyl groups attached to carbon atoms 1: and 2: The result with (c) appears to show that the hydroxyl groups on atoms 5: and 6: have little to do with the increase in conductivity. It is to be noted also that 3:4:5:6-tetramethyl mannitol, though an α-glycol, differs from the glycols previously mentioned, e.g.

*Reciprocal ohms(mhos) are the units used throughout.

glycol and glycerol, in that it exerts a marked positive influence on the conductivity of boric acid.

Irvine next examined several methylated glucoses: he found that tetramethyl methylglucoside gave an increase in conductivity when added to boric acid. Böeseken and Couvert[18] in 1921 found no such increase. In the same paper, Irvine gives details of his conductivity measurements on 2:3:4:6-tetramethyl glucose (2:3:5:6 on the basis of the then generally accepted configuration of glucose) He found that the conductivity of this substance in M/2 boric acid solution rose very rapidly, a considerable initial depression of conductivity giving place to a final exaltation of 130 x 10^{-6}, the change occupying three hours. As Irvine states, this was an unexpected result, since both α- and β-forms of tetramethyl glucose possess only one unsubstituted hydroxyl group, so that a mixture of the two forms, as at equilibrium, should have a conductivity of similar magnitude to that displayed by the individual forms.

Upon these facts, Irvine based a theory explaining the mechanism of mutarotation of such a compound: he states that "since the conductivity increases upon mutarotation, the latter must be accompanied by the formation of at least one additional hydroxyl group which assumes a position favourable for

combination with boric acid. Now in the fully methylated sugar there is only one possible way of satisfying this condition and that is by addition of water to the oxygen atom of the ring: the hydroxyl group so formed will then be adjacent to the hydroxyl group on the first carbon atom. Judging from the permanent final conductivity with boric acid, both forms of the sugar ultimately exist in solution as oxonium hydrates."

Böeseken and Couvert[18], however, find no such increase in conductivity when tetramethyl glucose is added to boric acid solution: the initial effect is a depression of conductivity, and the value undergoes little change. If this is so, then Irvine's theory loses its experimental support.

Kolthoff[19], in a paper on the "Interpretation of neutralisation curves of mixtures of boric acid and polyvalent alcohols", remarks that "although thanks to the work of Magnanini and more especially that of Böeseken and his pupils, it has long been known that polyvalent alcohols, through formation of a complex, strongly increase the acidity of a boric acid solution, nothing is known quantitatively of the stability of these complexes". It is usually assumed that increase of acidity is proportional to the stability of the complex formed, but from the work of

Verkade[20] on meconic and chelidonic acid it appears that such generalisations must be made with caution; this is not surprising, since increase of real acidity depends not only on the extent of complex formation but also on the dissociation constant of the complex. Again, Kolthoff[21] mentions that Böeseken and Verkade consider the decreased conductivities of solutions of acids which do not form complexes with boric acid to be indicative of diminution of the degree of ionisation: this, Kolthoff states, is unwarranted, since the authors do not take into account the repression of the dissociation of boric acid by the stronger acid.

Kolthoff, in the first paper, examines the neutralisation curves of alcohol-boric acid mixtures: he says that fructose as well as mannitol and other polyvalent alcohols form multibasic complex acids in which one molecule of polyvalent alcohol combines with more than one molecule of boric acid. He finds also that the composition of the complex is apparently dependent on the ratio of the two components in the solution: calculation of the dissociation constants of the complexes gives a value of 3×10^{-7} in the case of glycerol.

It has been noted by several observers[22] that certain organic hydroxy-acids are more soluble in a boric acid solution than in water itself: this,

according to Kolthoff, shows that "the complexes formed with boric acid are often fairly stable". A general rule evolved by Herz[23] states that "as a rule, a given acid is less soluble in a solution of a mineral or organic acid than it is in pure water: the decrease in solubility is considerably greater than that calculated from the displacement of the dissociation equilibria on account of the common ion".

Optical rotation has frequently been used as a means of investigating the reaction taking place, in solution, between boric acid and organic acids, alcohols etc.. It is well known that such optically inactive compounds as boric acid when added to solutions of the optically active modifications of malic and tartaric acids or their salts, produce a more or less marked alteration in the specific rotations of the solutions. Mannitol is a classic example of a substance which shows no rotatory power in aqueous solution until boric acid is added, when a notable dextro-rotation is observed. Thus Irvine[17] records a practically zero rotation for mannitol in aqueous solution, whilst in M/2 boric acid solution the rotation was $+28.3^{\circ}$.

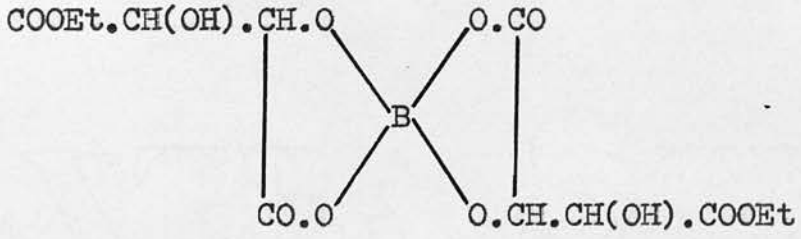
This change in optical rotation was also mentioned by Burgess and Hunter[24] in their paper on borotartaric acid: these authors also noted the increase of solubility of the boric and tartaric acids in the

presence of one another as compared with their original solubilities in water.

Optical measurements were carried out by Henderson and Prentice[25] on boric acid and potassium lactate: the lactate alone had a specific rotation $[\alpha]_D^{20^\circ} = +10.05^\circ$: on the addition of boric acid, a fall in rotation was observed, a minimum value of -2.83° being obtained when the lactate and boric acid were present in the ratio 1:1, i.e., in such proportions as would be required for the formation of a salt such as $CH_3CHO(BO).COOK$ — a potassium borolactate. The decrease in rotation was not due merely to liberation of lactic acid, because the rotation was much greater than that of a solution of lactic acid of equivalent strength and moreover boric acid also has a marked effect on the rotation of a solution of lactic acid itself.

Henderson and Prentice came to the conclusion that "these alterations in rotation — with malic, tartaric and lactic acids, as with certain other substances — must be due to the formation of new optically active compounds, because in many cases the substances whose existence is indicated by the rotations of their solutions, could be obtained in the solid state". Sodium arsenite will also induce a change in rotation in the same way as borax[26] . Change of acidity and of rotation provide means for the estimation of mannitol[27].

Darmois[28] carried out a series of researches on the influence of boric acid on the rotatory power of malic and tartaric acids. He examined the rotations of mixtures of boric and malic acids and concluded that the results showed the existence of two series of complexes. With boric acid and tartaric acid he obtained evidence of a dextro-rotatory complex in solution: strongly alkaline solutions contained a laevorotatory complex. The laevorotatory series of complexes gave rise to crystalline salts of Sodium, Ammonium and Aniline of the form $H_3BO_3.3C_4H_5O_5M$. In his third paper Darmois, by the addition of sodium metaborate to ethyl tartrate solutions, found evidence of a complex to which he assigned the formula

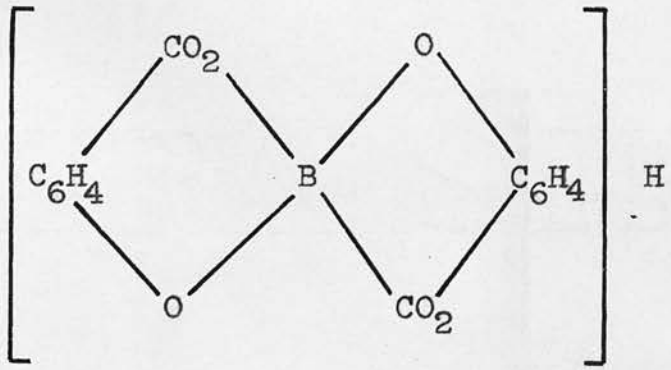


Several workers, notably Bancroft and Davis[29], have doubted the existence, even in solution, of any such complexes as formulated by Böeseken and others: they attributed the increased acidity of boric acid to its increased dissociation in presence of the organic compounds in the solution, whilst the change in optical rotation was ascribed to the abnormal effect of boric acid solutions. The chief objection of

Bancroft and Davis to the acid complexes proposed by Böeseken was the difficulty of isolating any such complex in the solid state, many of the compounds claimed to have been isolated being of doubtful authenticity. For example, a substance supposed to be a compound of glycerol and boric acid in the ratio of 1:1 was shown to be merely boric acid with glycerol adsorbed and thereby difficult to remove, which fortuitously analysed to an exact ratio. The mannitoboric acid of Fox and Gauge[30] could not be reproduced and its existence is therefore in doubt. Hildebrand[39] carried out titrations of boric acid using mannitol in increasing proportion up to 3 mols. mannitol. With each addition of mannitol, the boric acid curve looked more like that of a strong acid, the vertical portion being displaced to lower pH values and increasing in length so that titration using phenolphthalein as indicator becomes feasible. There was no indication, however, that 3 molecules of mannitol represented the end of the process and even this ratio is opposite to that used by van't Hoff in suggesting his original ring structure. Catechol, pyrogallol and other compounds which Böeseken showed to increase the conductivity of boric acid gave no vertical portion at all.

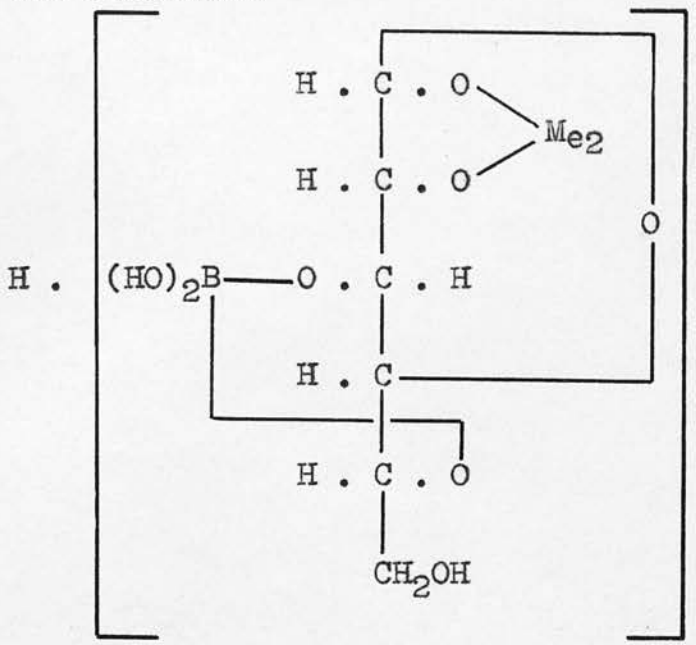
Numerous other papers have been published raising objections to the theory of complex formation.

There have been prepared, however, a number of compounds of boric acid and hydroxy-compounds whose existence is certain. Lowry[31] has prepared a borotartaric acid $KB(C_4H_4O_6)_2$: Böeseken and Vermaas[32], in a paper replying to that of Bancroft and Davis, describe a number of definite anions containing boron, which have been isolated in the form of salts. Hermans[33] reports the preparation of a number of compounds, important among them being his disalicyl-boric acid: this work found remarkable confirmation by Meulenhoff's[34] resolution of this acid into its optical antipodes. Hermans gave the acid the formula



Among the sugar and sugar-alcohol compounds claimed to have been prepared are the glucose diboric acid of Brigl and Grüner[35], the α-methylglucoside diborate of Bell[36] and the mono-acetone monoborate compounds of glucose and of mannitol isolated by von Vargha[37]: the latter suggested as the formula of the glucose compound/

compound the structure:



von Vargha actually isolated solid substances, but the experimental evidence in support of a compound of the above form is slight: melting-points are indefinite.

Recently Srinivasan and Sreenivasaya[38] have attempted to demonstrate the actual formation of boric acid complexes by dilatometric methods: they measured the increase in volume expansions when solutions of mannitol and sorbitol were added to boric acid solution, and concluded that these volume expansions, which showed a definite relationship to the concentration of mannitol and sorbitol present, suggested the formation of compounds such as those suggested by Böeseken.

Conclusion.

It will be obvious from the varied methods of approach enumerated above, that the problem of what takes place when a substance such as mannitol is added to a solution of boric acid, opens up a wide field for research. In spite of the number and variety of physico-chemical measurements such as optical rotation, electrical conductivity, hydrogen-ion concentration and phase study, which have been carried out, a satisfactory and conclusive answer has yet to be found.

The work described in the following pages is confined, in the main, to a study of the effect of certain sugars and sugar derivatives on the conductivity of boric acid solution, and an attempt is made to correlate the results with the number and position of the hydroxyl groups and also with the configuration of the molecule as a whole.

Bibliography.

1 Klein.....Bull. Soc. Chim.1878 39 178

2 Berenschtein & Ajzenberg.Ukrain. Chem.J. 1933 8 307

3 Thomas & Kalman.....Compt. rend. 1933 196 1672

4 Voicu & Axente.....Bull. Soc. Chim. România, 1930 12 61

5 Jones.....Am. J. Sci. 1899 7 147; 8 127

6 Berenstein.....Biochem. Z. 1929 215 344

7 van't Hoff....."Lagerung der Atome in Raume" 2nd.Edn., p.133

8 Magnanini.....Zeit. physik. Chem. 1890 6 58; Gazzetta, 1892 22 541; 1893 23 197

9 Ageno & Valla.....Chem. Ztg. 1913 36 221

Gazzetta, 1913 43 163

10 Böeseken.....Rec. Trav. chim.1911 30 392

11 Derx.....ibid. 1922 41 327

12 Böeseken.....ibid. 1915 34 96

13 Micheel & Micheel.....Ber. 1930 63 386

14 Vavon.....Bull. Soc. Chim. 1931 49 997, 1011

Armstrong.....Proc. Lond. 1904 74 188

15 Freudenberg, Helferich & Winkler...Zeit. physiol. Chem. 1932 209 270

16 Böeseken & Couvert.....Rec. Trav. chim.1921 40 369

Verschuur.....ibid. 1928 47 455

17 Irvine & Steele.....J.C.S. 1915 107 1221

18 Böeseken & Couvert.....Rec. Trav. chim.1921 40 354

19 Kolthoff.....Rec.Trav.chim. 1925 44 975

20 Verkade.....ibid. 1924 43 879

21 Kolthoff.....ibid. 1926 45 394

22 Verkade.....ibid. 1924 43 879

Kolthoff.....ibid. 1926 45 607

23 Herz.....Z. anorg. Chem.1903 34 205

ibid. 1910 66 93

ibid. 1911 70 70

24 Burgess & Hunter.....J.C.S. 1929, 2838

25 Henderson & Prentice.....ibid. 1902 81 658

26 Vignon.....Bull. Soc. Chim.1873 20 532

27 Muller.....ibid. 1894 11 329

Badreu.....J. pharm. chim. 1921 24 12

28 Darmois.....J. chim. phys. 1926 23 130, 649

ibid. 1930 27 179

29 Bancroft & Davis.....J.Phys. Chem. 1930 34 2479

30 Fox & Gauge.....J.C.S. 1911 99 1075

31 Lowry.....ibid. 1929, 2853

32 Böeseken & Vermaas.....J.Phys. Chem. 1931 35 1477

33 Hermans.....Verslag Akad.Wet.Amsterdam, 1923 31 626

Z.anorg. Chem. 1925 142 83

34 Meulenhoff.....Dissertation, Delft, 1924

35 Brigl & Grüner.....Ann., 1932 495 60

Ber, 1932 65 641

36 Bell.....J.C.S. 1935 175

37 von Vargha.....Ber. 1933 66 704, 1394

38 Srinivasan & Sreenivasaya.J.Phys. Chem. 1934 38 703

Part Two

E X P E R I M E N T A L

CONDUCTIVITY EXPERIMENTS

The Wheatstone Bridge method of measuring conductivities was employed throughout. To give greater accuracy, a cylindrical bridge, wound with 3.6 metres of wire and marked off into 1000 equal divisions, was employed.

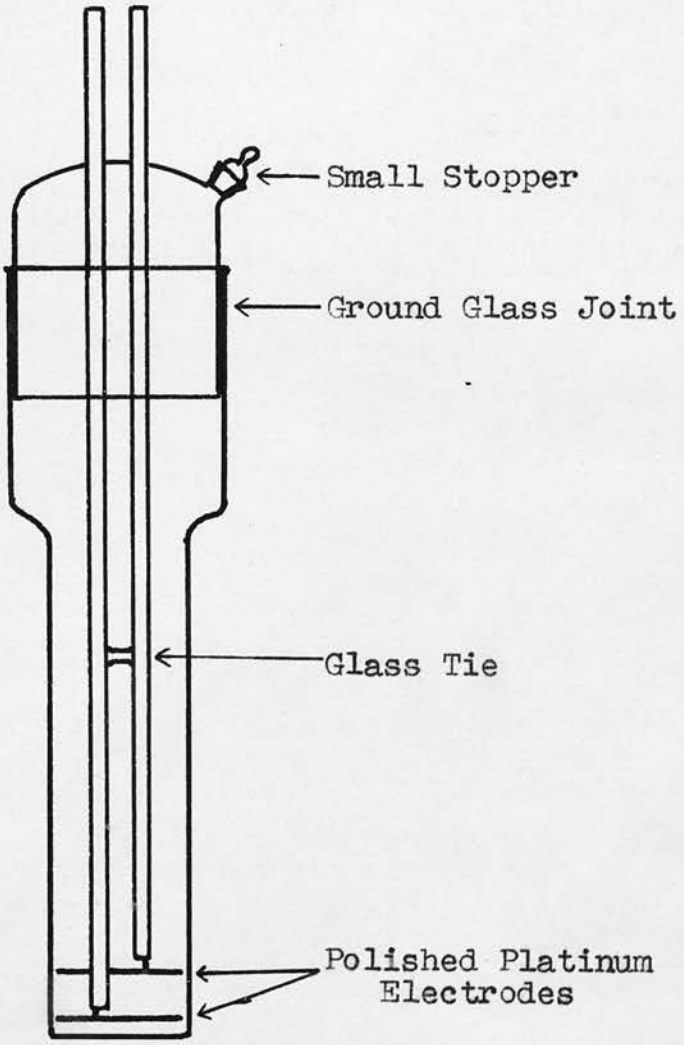
Some trouble was experienced when a conductivity cell of normal pattern was used: it was found that even when the electrodes were freshly platinised, and the whole cell carefully steamed out and washed, the conductivities of solutions of low conductivity, such as the sugars and pure water itself, rose rapidly with time. By burning off the Platinum Black, thus giving a grey metallic surface, the results were decidedly improved, but still showed a fairly considerable rise in a short time. Since the cell-cover was loose-fitting, being merely laid on top of the cell, the rise may have been due in part to contamination of the solution from the atmosphere.

It was decided, therefore, to have a closed cell made to specification in order to remedy as far as possible these defects. The cell was constructed completely of Pyrex Glass by the Pyrex Co.. The electrodes were of polished platinum and the body of the cell of such a size that 1 c.c. of solution was

easily sufficient to cover the electrodes: the top, with a small stoppered opening, fitted into the body by means of a ground-glass joint.

The polished plates were found to be very satisfactory: they gave a sharp minimum point on the bridge with the solutions employed in this series of experiments.

Diagram of Cell



Procedure for Measurement of Conductivities.

For purposes of economy in the case of substances difficult to obtain, and also to reduce chances of contamination to a minimum, all solutions for conductivity work were made up in the cell itself. The latter, having been steamed out and thoroughly washed, was rinsed with absolute alcohol and dried in an oven at 60°C: the alcohol itself had a very low conductivity, namely 0.5×10^{-6}*. The cell was then weighed and a weight of substance introduced equivalent to 1c.c. of M/2 solution, e.g. 0.0900g. exactly in the case of glucose.

1c.c. of conductivity water or M/2 boric acid was then added from a pipette, the cell gently agitated to effect solution and put immediately into the thermostat. The time at which the water or boric acid was added was noted, and the first conductivity reading was usually taken 10 minutes from that time.

This method of making up the solutions obviously did not give an exactly M/2 solution, being slightly less than M/2, but the error was very small and in any case every solution was made in the same way, so that the comparison of results was in no way affected.

A temperature of $25^{\circ} \pm .03^{\circ}$ was employed throughout.

* Reciprocal ohms (mhos) were the units employed throughout.

Calibration of the Bridge

The bridge was calibrated throughout its length before use.

R_1 ω	R_2 ω	Bridge Reading	Theoretical Reading	Correction
500	3500	125.00	125.00	0.00
750	3250	187.50	187.50	0.00
1000	3000	250.50	250.00	-0.50
1250	2750	313.00	312.50	-0.50
1500	2500	375.50	375.00	-0.50
1750	2250	438.00	437.50	-0.50
2000	2000	500.50	500.00	-0.50
2250	1750	563.00	562.50	-0.50
2500	1500	625.75	625.00	-0.75
2750	1250	688.25	687.50	-0.75
3000	1000	751.00	750.00	-1.00
3250	750	813.50	812.50	-1.00
3500	500	876.25	875.00	-1.25
3750	250	938.75	937.50	-1.25

In taking the conductivity readings, a suitable resistance, usually 1000 - 3000ω, was inserted and the bridge rotated until the position of minimum sound was obtained. The bridge reading was taken to 0.25 of a scale division, i.e. 1/4000 of the bridge length: after correction of this reading from the calibration table, the conductivity was calculated in the usual way, knowing the cell constant.

Example of calculation of specific conductivity (k) :

If resistance inserted is R and the bridge reading is x, then the specific conductivity, k, is given by

$$k = \frac{K \times (1000 - X)}{R \times X} \text{ mhos}$$

where K is the cell constant.

Cell Constant

Using N/500 KCl, ($k = .2926 \times 10^{-3}$)

Resistance Box	Bridge Readings				Cell Resistance ω
	1	2	Mean	Corrected	
3000 ω	333.0	332.5	332.75	332.25	1492
2000	428.5	428.0	428.25	427.75	1496
1500	500.0	499.5	499.75	499.25	1496
1000	600.5	599.5	600.00	599.25	1494
750	682.5	682.0	682.25	681.50	1497
500	751.0	750.0	750.50	749.50	1496
300	834.5	834.0	834.25	833.25	1498

Mean Resistance = 1496 ω

K (cell constant) = $1496 \times .2926 \times 10^{-3}$

$= \underline{.4378}$

This cell constant did not vary throughout the whole series of conductivity experiments. A somewhat larger cell of the same type was used in the measurements on glucose solutions. Owing to the greater chance of movement of the larger plates, the cell constant was inclined to vary slightly and was determined separately for each experiment.

Elevation or Depression of Conductivity

is found as follows:- when a pure sample of a non-electrolyte such as a sugar is added to boric acid which normally is only feebly ionised, then the resultant conductivity should approximate to the sum of the respective conductivities of the two substances. The difference between this figure and that actually found by experiment for the mixture, will give the elevation or depression, according as the experimental figure is greater or less than the calculated sum of the conductivities.

The specific conductivity of the water used in the following experiments was $1.9\text{-}2.0 \times 10^{-6}$. Being comparatively very small, it was neglected in the calculations.

Preparation of α-d-Glucose.

α-d-glucose was prepared according to the method of Hudson and Dale[1]:-

100g. pure glucose were dissolved in 50ccs. of water, warming on a water-bath to facilitate solution. When completely dissolved, the source of heat was removed and 200ccs. of cold glacial acetic acid were added with thorough stirring: crystallisation was slow, due to the presence of water. The α-glucose was filtered off and washed first with 90% ethyl alcohol and then with absolute alcohol.

$[\alpha]_D^{20°}$/2 mins.= + 106° (c= 3.0 in water)

The specimen of α-glucose so prepared was found to have a specific conductivity, in M/2 solution, of 80 x 10^{-6}: this comparatively high value would be due to traces of acetic acid in the final product. Repeated washing with alcohol had no marked effect on the conductivity, at any rate not lowering it sufficiently for our purpose. It was found that the best way of bringing down the value was to thoroughly grind the glucose with cold pyridine, in which it partially dissolved, re-precipitate with absolute alcohol, filter, and wash with alcohol until all traces of pyridine were completely removed. The glucose was finally freed from solvent by warming in a vacuum.

This method in no way affected the rotatory power of the glucose.

Conductivities of α-d-Glucose

M/2 aqueous solution:

$k \times 10^6 = 11.5$

M/2 solution in M/2 boric acid:

$R = 1000\omega$, $K = 0.3443$

Minutes	Corrected Bridge Reading	$k \times 10^6$
5	780.00	96.3
10	782.75	94.7
15	785.50	93.2
20	787.75	91.9
30	791.75	89.8
40	794.50	88.3
60	798.75	86.0
80	801.25	84.7
100	802.75	83.8
110	803.25	83.6
120 (equil.)	803.75	83.3

initial value, by extrapolation $= 98.5 \times 10^{-6}$

M/2 boric acid alone is 27.6×10^{-6}

Elevation of Conductivity $= 59.4 \times 10^{-6}$ (initial)

and 44.2×10^{-6} (final)

Preparation of β-d-Glucose.

β-d-glucose was prepared by the method of Behrend[2]:-

12g. pure glucose were dissolved in 30g. dry pyridine at the boiling point, and when solution was complete, boiling was continued for a further 10 minutes. The solution was then shaken for 32 hours and allowed to stand a further 14 hours: the crystals formed were filtered off, washed with a little pyridine, then washed thoroughly with absolute alcohol till all traces of pyridine were removed. Final removal of solvent was effected by warming for some time in a vacuum.

$[\alpha]_D^{20°}$/3mins.= +19.5° (c = 1·5 in water)

The specimen of β-d-glucose so prepared was found to be sufficiently pure for conductivity measurements.

Conductivities of β -d-Glucose

M/2 aqueous solution:

$k \times 10^{6} = 8.5$

M/2 solution in M/2 boric acid:

$R = 1000\omega \quad K = 0.3395$

Minutes	Corrected Bridge Reading	$k \times 10^{6}$
12	836.00	66.6
15	834.25	67.5
20	832.50	68.3
30	829.00	70.0
40	826.00	71.5
60	822.75	73.1
80	820.75	74.1
100	819.50	74.8
110	819.25	74.9
120 (equil)	819.00	75.0

initial value, by extrapolation $= 63.0 \times 10^{-6}$

M/2 boric acid alone is 28.0×10^{-6}

Elevation of conductivity $= 26.5 \times 10^{-6}$ (initial)

and 38.5×10^{-6} (final)

Further Experiments on α-and β-d-Glucose

This series of experiments was carried out in order to see whether there was any difference in the equilibrium conductivity figures for M/2 α-and β-glucose solutions when the boric acid was added after attainment of equilibrium instead of at the beginning.

The experiments were carried out in such a way that the final solutions on which the conductivity measurements were carried out represented M/2 glucose in M/2 boric acid.

Procedure:

(1) 4.5g. α-glucose were weighed out into a 50c.c. flask; water was then run in from a burette and the glucose dissolved before finally making up to the mark. This was merely a measure of the volume of solvent required for 50c.cs. solution. The volume required was 47.1c.cs.

Now 100c.cs. M/2 boric acid contain 3.090g. boric acid

47.1 " " " " " 1.455g. " "

Thus for an M/2 solution of glucose in M/2 boric acid, water containing 1.455g. boric acid will have to be added to a glucose solution in the flask.

(2) 4.5g. α-glucose were weighed out in the flask and 20ccs. conductivity water were added: this solution was set aside and allowed to come to equilibrium (24 hours) before proceeding further.

(3) A solution of boric acid containing 1.455g. in 25c.cs. was made up; 25c.cs. of this were then added to the equilibrium glucose solution which was made up exactly to the mark and shaken thoroughly. We thus have finally an M/2 glucose solution in M/2 boric acid.

(4) A conductivity reading was taken on the solution and gave $\underline{81.5 \times 10^{-6}}$.

An exactly similar experiment was carried out for β-glucose: the conductivity of the equilibrium solution in boric acid was in this case $\underline{74.8 \times 10^{-6}}$.

Note to (1):-

Since water was used in the burette, 47.1c.c. will not represent accurately the volume of boric acid solution required, but this figure will be near enough not to affect the conductivity results to any marked extent.

Mutarotation of α- and β-d-Glucose in Aqueous and in Boric Acid Solutions.

M/2 aqueous α-glucose			M/2 α-glucose in M/2 boric acid	
Minutes	Corrected Polarimeter Reading	$[\alpha]_D^{20°}$	Corrected Polarimeter Reading	$[\alpha]_D^{20°}$
5	9.74	+108.2°	9.75	+108.3°
10	9.50	105.5	9.46	105.1
15	9.20	102.2	9.20	102.2
20	8.95	99.4	8.93	99.2
30	8.47	94.1	8.46	94.0
40	8.07	89.7	8.08	89.8
60	7.43	82.6	7.45	82.8
80	6.86	76.2	6.87	76.3
100	6.44	71.6	6.45	71.7
140	5.80	64.4	5.83	64.8
180	5.39	59.9	5.37	59.7
220	5.18	57.6	5.17	57.4
240	5.08	56.4	5.08	56.4
280	4.94	54.9	4.92	54.7
equil.	4.74	+ 52.7°	4.73	+ 52.6°

Similar experiments were carried out on M/4 and M/8 α-d-glucose in aqueous and in M/2 boric acid solution: the figures in each case showed the same rate of mutarotation in aqueous and boric acid solution: the equilibrium values only varied from 52.3-52.6°.

	M/2 aqueous β-glucose		M/2 β-glucose in M/2 boric acid	
Minutes	Corrected Polarimeter Reading	$[\alpha]_D^{20°}$	Corrected Polarimeter Reading	$[\alpha]_D^{20°}$
3	1.85	+ 20.6°	1.87	+ 20.8°
6	1.95	21.7	1.92	21.3
10	2.07	23.0	2.08	23.1
15	2.20	24.4	2.22	24.7
20	2.31	25.7	2.32	25.8
30	2.56	28.4	2.56	28.4
40	2.75	30.6	2.77	30.8
60	3.11	34.6	3.13	34.8
75	3.33	37.0	3.35	37.2
90	3.53	39.2	3.53	39.2
120	3.80	42.2	3.81	42.3
150	4.02	44.7	4.02	44.7
180	4.15	46.1	4.14	46.0
240	4.41	49.0	4.43	49.2
equil.	4.70	+ 52.2°	4.71	+ 52.3°

Conductivities of α-d-Galactose

The galactose used was Kerfoot's "Pure" : this was found to be entirely α-galactose.

Mutarotation: (in aqueous solution c = 1.3)

Minutes	Corrected Polarimeter Reading	$[\alpha]_D^{20°}$
3	+ 1.77	+ 137.8°
5	1.74	135.5°
12	1.68	130.9°
20	1.62	126.2°
45	1.48	115.3°
⋮	⋮	⋮

This gives an initial value, by extrapolation, of + 140°

Before taking conductivities, the galactose was washed with 90% ethyl alcohol and thoroughly dried in a vacuum.

(For conductivity readings see next page)

M/2 aqueous solution:

$k \times 10^6 = 23.3$

M/2 solution in M/2 boric acid:

$R = 1000\omega \qquad K = .4378$

Minutes	Corrected Bridge Reading	$k \times 10^6$
10	843.25	81.4
20	846.00	79.7
30	847.75	78.6
40	849.75	77.4
50	851.00	76.7
60	852.00	76.1
80	853.25	75.3
100 (equil.)	853.50	75.2

Initial value, by extrapolation $= 83.7 \times 10^{-6}$

M/2 boric acid alone was 30.9×10^{-6}

Elevation of Conductivity $= 29.5 \times 10^{-6}$ (initial)

and 21.0×10^{-6} (final)

Conductivities of β-d-mannose.

All the samples of mannose tried possessed a high conductivity in aqueous solution: a recrystallisation of the best specimen was not effective in reducing the conductivity to any appreciable extent.

$[\alpha]_D^{18^\circ}$ = -17.0°(initial) $\longrightarrow$ $+14.8^\circ$(final), (c = 3.0 in water)

M/2 aqueous solution:

$k \times 10^6 = 78.2$

M/2 solution in M/2 boric acid:

(R = 2000ω, K = .4378)

Minutes	Corrd. Bridge Reading	$k \times 10^6$
7	670.00	107.8
10	670.75	107.5
15	672.00	106.9
30	673.50	106.1
40	674.00	105.9
50 (equil.)	674.25	105.8

Initial value = 108.6×10^{-6}

M/2 boric acid alone was 30.0×10^{-6}

Initial elevation of conductivity = 0.4×10^{-6}

Final depression of conductivity = 2.4×10^{-6}

Conductivities of α-l-rhamnose.

Specimen supplied by British Drug Houses Ltd., in the form of rhombic crystals. The rhamnose was finely powdered and used without further treatment. $[\alpha]_D^{18°}$/3 mins = − 6·8° ⟶ + 9·0° (final) (c = 1.0 in water)

M/2 aqueous solution:

$k \times 10^6 = 5.2$

M/2 solution in M/2 boric acid:

$k \times 10^6 = 43.7$ (initial) ⟶ 48.1 (final)

M/2 boric acid alone was 31.0×10^{-6}

Elevation of Conductivity = 7.5×10^{-6} (initial)

and 11.9×10^{-6} (final)

Conductivities of Sucrose:

A.R. Specimen from British Drug Houses Ltd., finely powdered and used without further treatment.

M/2 aqueous solution:

$$k \times 10^6 = 7.8$$

M/2 solution in M/2 boric acid:

$$k \times 10^6 = 29.2$$

M/2 boric acid alone was 30.9×10^{-6}

Depression of Conductivity $= 9.5 \times 10^{-6}$

Conductivities of Inositol:

Specimen from Departmental Museum, used without preliminary treatment.

$[\alpha]_D^{16^\circ}$ in water was zero: the inositol was therefore the symmetrical form.

M/2 aqueous solution:

$$k \times 10^6 = 21.0$$

M/2 solution in M/2 boric acid:

$$k \times 10^6 = 37.5$$

M/2 boric acid alone was 30.9×10^{-6}

Depression of Conductivity $= 14.4 \times 10^{-6}$

Preparation of α-Methylglucopyranoside.

α-methylglucopyranoside was prepared according to the method of Paterson and Robertson[4]: It was recrystallised 5 times from absolute alcohol.

m.p. 167°. $[\alpha]_D^{20^\circ} = +159^\circ$ (c = 3.0 in water).

OMe; Found, 15.4%; Calc. for $C_7H_{14}O_6$, 16.0%.

Conductivities of α-Methylglucopyranoside

M/2 aqueous solution:

$k \times 10^6 = 3.9$

M/2 solution in M/2 boric acid:

$k \times 10^6 = 22.5$

M/2 boric acid alone was 27.9×10^{-6}

Depression of Conductivity $= 9.3 \times 10^{-6}$

Preparation of α-Methylgalactopyranoside.

α-methylgalactopyranoside was also prepared by the method of Paterson and Robertson[4].

It was twice recrystallised from absolute alcohol.

m.p. 116° $[\alpha]_D^{20°} = +179°$ (c = 1.0 in water)

OMe; Found, 15.9%; Calc. for $C_7H_{14}O_6$, 16.0%

Conductivities of α-Methylgalactopyranoside.

M/2 aqueous solution:

$k \times 10^6 = 12.9$

M/2 solution in M/2 boric acid:

$k \times 10^6 = 39.8$

M/2 boric acid alone was 30.9×10^{-6}

Depression of Conductivity $= 4.0 \times 10^{-6}$

Preparation of 2:3:4:6-Tetramethyl Glucose.

The tetramethyl glucose was prepared according to the method of West and Holden[5], with slight variations.

Tetramethyl methylglucoside was first prepared, following exactly the procedure of West and Holden, who then hydrolysed this to tetramethyl glucose by means of 2N HCl and a vigorous current of steam: though quicker, this method was found to be no more effective or convenient than heating in a water-bath at 90° with 2N HCl for 5 to 6 hours. Pure charcoal may be added during the hydrolysis.

After hydrolysis, whichever method was used, the solution was saturated with sodium sulphate and extracted with chloroform four or five times. The syrup obtained on evaporation crystallised spontaneously on cooling: if crystallisation is not immediate it can be induced by adding light petroleum (40/60°) and stirring vigorously.

The tetramethyl glucose was recrystallised from warm light petroleum/ether (100:1); needleshaped crystals are formed on cooling.

m.p.85°-88° (slow heating: see also under conductivities)

OMe; found 51.5%; Calc. 52.5%

Conductivities of 2:3:4:6-Tetramethyl Glucose.

An initial conductivity experiment on an M/2 aqueous solution showed a conductivity of about 50×10^{-6}: as this value was somewhat higher than that of other substances under examination, an attempt was made to purify the tetramethyl glucose further. It was rapidly distilled at 135° (bath temp.) / 0.03mm., and the conductivity was now found to be 40×10^{-6}. As distillation obviously reduced the conductivity considerably, 2g. of tetramethyl glucose was redistilled five times, care being taken to have the apparatus scrupulously clean. This proved successful, as can be seen from the conductivity figures.

m.p.72°, $[\alpha]_D^{20°}$/3 mins. $= +70.3° \longrightarrow +79.8°$ (equil.)

(c = 0.5 in water) [cf. Boeseken[14], + 79.82°]

The specimen was thus the β-form.

M/2 aqueous solution:

$k \times 10^6 = 7.0$

M/2 solution in M/2 boric acid:

$k \times 10^6 = 20.8$

M/2 boric acid alone was 27.9×10^{-6}

Depression of Conductivity $= 14.1 \times 10^{-6}$

Preparation of 2:3:4:6-Tetramethyl Methylglucoside.

Tetramethyl methylglucoside was prepared according to the method of West and Holden[5]: the syrup was twice distilled at 85°/0.04 mm., using a fractionating column. $\eta_D^{18°} = 1.4465$.

OMe; Found, 60.5%; Calc. for $C_{11}H_{22}O_6$, 62.0%

Conductivities of Tetramethyl Methylglucoside.

M/2 aqueous solution:

$k \times 10^6 = 12.2$

M/2 solution in M/2 boric acid:

$k \times 10^6 = 21.5$

M/2 boric acid alone was 27.6×10^{-6}

Depression of Conductivity $= 18.3 \times 10^{-6}$

Preparation of 2:3:6-Trimethyl Methylglucopyranoside.

Starch was methylated according to Haworth, Hirst and Webb[6] until the methoxyl content reached 44%: hydrolysis was then effected by means of 2% methyl-alcoholic-HCl after the method of Baird, Haworth and Hirst[7]. The mixture of tri- and tetramethyl methyl glucosides so obtained was slowly fractionated several times in a high vacuum, the first portions of the distillate, consisting of the tetramethyl glucose fractions, being set aside. Finally a colourless syrup was obtained. $\eta_D^{18^\circ} = 1.4550$

OMe; Found, 51.5%; Calc. for $C_{10}H_{20}O_6$, 52.5%

Conductivities of 2:3:6-Trimethyl Methylglucopyranoside.

M/2 aqueous solution:

$k \times 10^6 = 14.1$

M/2 solution in M/2 boric acid:

$k \times 10^6 = 25.5$

M/2 boric acid alone was 27.6×10^{-6}

Depression of Conductivity $= 16.2 \times 10^{-6}$

Preparation of 2:3:6-Trimethyl glucopyranose

The trimethyl methylglucoside prepared as described above was hydrolysed by means of 5% aqueous hydrochloric acid, and the sugar isolated in the usual manner.

After recrystallisation from ether it gave

$[\alpha]_D^{18^\circ} = +66^\circ$ (equil. value in water, c = 1.4)

m.p. 117°

OMe; Found, 40.5%; Calc. for $C_9H_{18}O_6$, 41.8%

Conductivities of 2:3:6-Trimethyl glucopyranose.

M/2 aqueous solution:

$k \times 10^6 = 10.4$

M/2 solution in M/2 boric acid:

$k \times 10^6 = 28.8$

M/2 boric acid alone was 27.9×10^{-6}

Depression of Conductivity = 9.5×10^{-6}

Preparation of 3:4:6-trimethyl α-mannopyranose.

3:4:6-trimethyl α-mannopyranose was prepared according to the method of Bott, Haworth and Hirst[3]:

(a) penta-acetyl mannose was obtained by the action at 0° for 4 days of acetic anhydride (100c.cs.) on mannose (20g.) in pyridine solution (100c.cs.)

(b) the penta-acetyl mannose was treated at 0° with glacial acetic acid saturated with hydrogen bromide, giving tetra-acetyl mannosidyl bromide.

(c) this was converted to "γ"-tetra-acetyl methyl-mannoside by shaking in dry methyl alcohol solution with silver carbonate; after one recrystallisation from ether, the crystals gave m.p. 98°, $[\alpha]_D^{20°} =$ -25° (c = 1.5 in chloroform)

(d) monoacetyl methylmannoside was obtained by deacetylating the "γ"-tetra-acetyl methylmannoside with excess N/2 alcoholic sodium hydroxide at 0° for 16 hours, and after neutralisation with carbon dioxide, extracting with cold ethyl acetate.

(e) The monoacetyl methylmannoside was fully methylated by means of silver oxide and methyl iodide yielding monoacetyl trimethyl methylmannoside. Four methylations of 6 hours each were given.

(f) The fully methylated syrup was then hydrolysed with N/2 HCl for 90 minutes in a water-bath at 90°. After neutralisation and extraction with chloroform, crystalline 3:4:6-trimethyl α-mannopyranose was obtained. 1.5g. recrystallised material was obtained from 5g. "γ"-tetra-acetyl methylmannoside.

After one recrystallisation from ether the crystals melted sharply at 104°.

$[\alpha]_D^{20°} = +22°$ (initial) $\rightarrow +8.3°$ (final)* (c = 0.6 in water)

Found; C, 48.5; H, 8.1; OMe, 41.0 %

Calc. for $C_9H_{18}O_6$; C, 48.7; H, 8.1; OMe, 41.8 %

Notes on the Preparation.

(a) Some difficulty was experienced in this preparation, due apparently to the rupture of the 1:2 ring by traces of acid during the deacetylation and methylation of the "γ"-tetra-acetyl methylmannoside: accordingly a trace of sodium bicarbonate was introduced into the extracts of mono-acetyl methylmannoside and mono-acetyl trimethyl methylmannoside before evaporation.

(b) Better results were obtained by using, in the methylations, silver oxide which had been prepared from barium hydroxide and not from sodium hydroxide: the resulting syrup then did not have the same tendency to reduce Fehling's solution.

*The same figures were obtained in boric acid solution.

Conductivities of 3:4:6-trimethyl ∝-mannopyranose.

The trimethyl mannose used was once recrystallised from ether.

M/2 aqueous solution:

$k \times 10^6 = 18.0$

M/2 solution in M/2 boric acid:

$R = 3000\,\omega$ $K = .4378$

Minutes	Corrected Bridge Reading	$k \times 10^6$
6	807.50	34.8
10	804.50	35.5
15	800.25	36.4
20	796.75	37.2
30	790.75	38.6
40	787.50	39.4
60	783.50	40.3
80	781.25	40.9-
90 (equil.)	781.00	40.9

initial value, by extrapolation $= 33.5 \times 10^{-6}$

M/2 boric acid alone was 27.6×10^{-6}

Depression of Conductivity $= 12.1 \times 10^{-6}$ (initial)

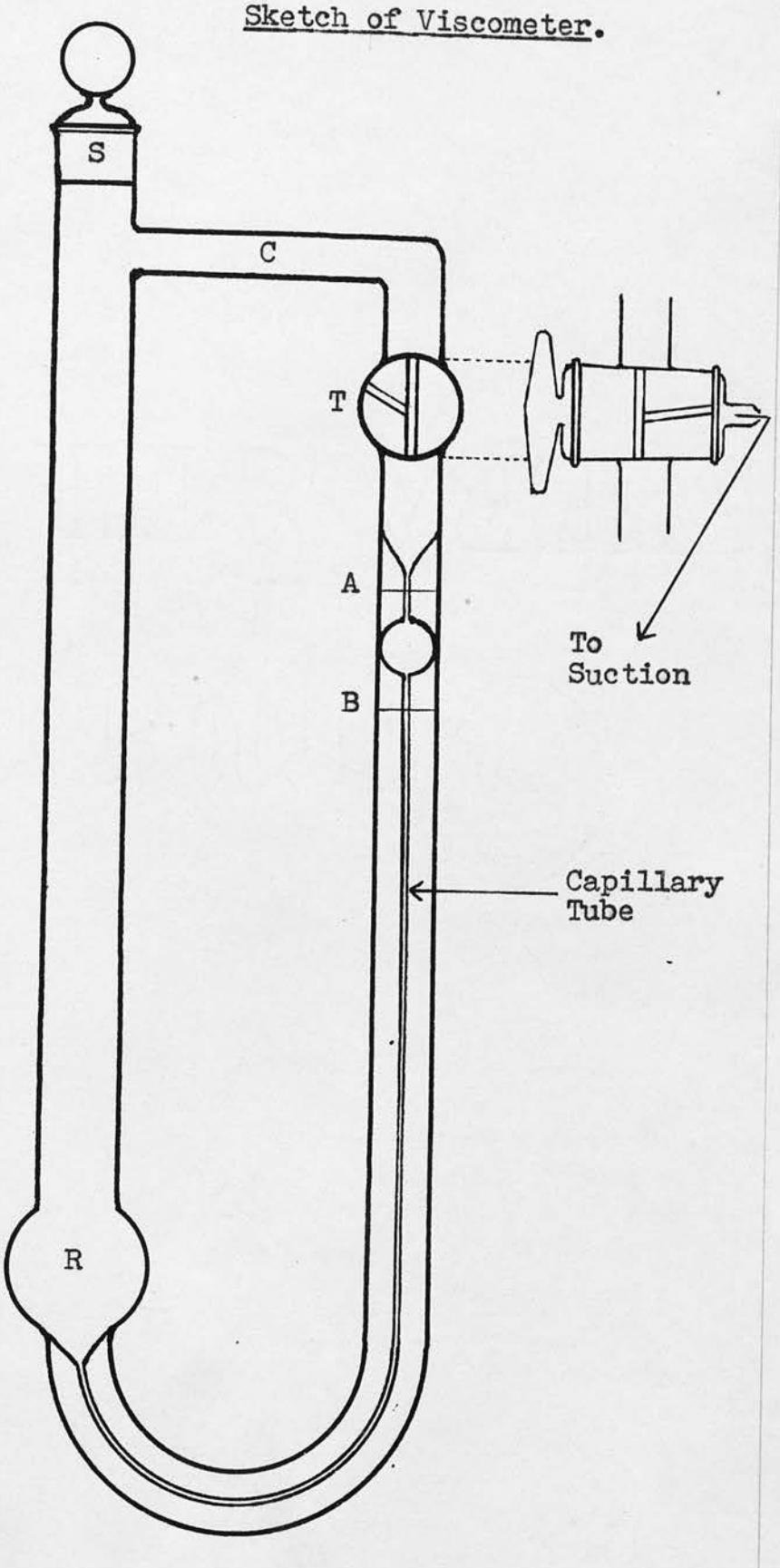
and 4.7×10^{-6} (final)

VISCOSITY MEASUREMENTS.

The apparatus used in these experiments was similar to that described by Hornel and Butler[8], namely a modification of the usual Ostwald viscometer having closed limbs connected by a cross-piece for equalising pressure in the limbs. The apparatus required less than 1cc. of liquid for a determination.

The particular viscometer used was constructed in the laboratory and the capillary was of such dimension that water required approximately 100 seconds to fall from A to B. (See diagram on next page)

Sketch of Viscometer.



Procedure:

The apparatus was thoroughly cleaned with chromic acid solution, washed with distilled water, rinsed with alcohol and dried by drawing a current of dust-free air through it: the capillary tube must be free from impurity of any kind, otherwise consistent readings cannot be obtained.

M/2 solutions of the substances to be examined were made up, in water and in M/2 boric acid. The viscometer was weighed and a certain volume of solution transferred by means of a pipette right into the bulb (R) of the apparatus, without allowing any liquid to come into contact with the sides of the limb. The apparatus was weighed again, giving the weight of a certain volume of solution.

The viscometer was then placed in a thermostat fitted with a glass window, the temperature being maintained at $25^{\circ} \pm .02^{\circ}$C. as for the conductivity experiments. When the viscometer had been in the thermostat for 10 minutes the liquid was drawn up by means of the two-way stopcock into the capillary limb above the upper of the two marks; the stopcock was then turned so as to connect the two limbs and the time of fall of the liquid between the two marks was noted, using a Venner stopwatch reading direct to 0.1 sec. The mean of several readings was used in every case.

The viscosity of the solution can then be calculated using the formula

$$\eta' = \eta \frac{\rho' T'}{\rho T}$$

where η and η' are the viscosity coefficients of two liquids of densities ρ and ρ' and times of fall T and T'. If T is determined for one liquid of known density ρ and viscosity coefficient η, then the viscosity η' of another liquid of density ρ' can be found by determining the time of fall T'.

Thus η' is obtained as a Relative viscosity whether η is taken as = 1 or whether its actual value is introduced into the equation.

In these experiments, water was taken as the standard, and $\eta = 1$: for the calculation of the relative viscosities, the weights of equal volumes of the liquids, as found above, were taken instead of the densities.

The glucoses and methylated sugars on which the measurements were carried out were the same specimens as employed in the conductivity experiments.

. Relative Viscosities.

M/2 aqueous solutions:

	Weight put into Viscometer	Mean Time of Fall (Seconds)	η_r
Water alone	0.9445g.	102.5	1.000
α-d-glucose	0.971	124.2	1.250
β-d-glucose	0.973	124.3	1.250
α-methylgluco-pyranoside	0.967	129.7	1.295
3:4:6-trimethyl α-mannopyranose	0.967	136.5	1.360
2:3:6-trimethyl methyl-glucopyranoside	0.962	140.7	1.400
2:3:4:6-tetramethyl glucose	0.962	139.5	1.390
2:3:4:6-tetramethyl methylglucoside	0.966	142.2	1.420
Boric acid	0.959	106.4	1.050

M/2 solutions in M/2 boric acid:

	Weight put into Viscometer	Mean Time of Fall (Seconds)	η_+
α-d-glucose	0.982g.	128.9	1.240
β-d-glucose	0.983	129.4	1.245
α-methylgluco-pyranoside	0.978	134.2	1.290
3:4:6-trimethyl α-mannopyranose	0.977	141.1	1.350
2:3:6-trimethyl methyl-glucopyranoside	0.972	146.6	1.400
2:3:4:6-tetramethyl glucose	0.973	145.4	1.390
2:3:4:6-tetramethyl methylglucoside	0.976	148.0	1.415

Preparation of glucose diethyl mercaptal.

Prepared according to the method of Fischer.[12]

The mercaptal was recrystallised from water and formed shining needle-like plates.

m.p. 128°

Conductivities of glucose diethyl mercaptal.

Glucose diethyl mercaptal is not very soluble in water and it was not found convenient to use solutions of greater strength than M/10: M/10 boric acid was also used in order to keep the molecular proportions the same as in the other conductivity experiments.

M/10 aqueous solution:

$$k \times 10^6 = 11.7$$

M/10 solution in M/10 boric acid:

$$k \times 10^6 = 193.0$$

M/10 boric acid alone was 5.1×10^{-6}

Elevation of Conductivity = 176.2×10^{-6}

Conductivities of Ethylene Glycol.

Specimen from British Drug Houses Ltd., used without any preliminary treatment.

M/2 aqueous solution:

$k \times 10^6 = 4.8$

M/2 solution in M/2 boric acid:

$k \times 10^6 = 27.1$

M/2 boric acid alone was 30.0×10^{-6}

Depression of Conductivity = 7.7×10^{-6}

Conductivities of Glycerol.

A.R. specimen.

M/2 aqueous solution:

$k \times 10^6 = 7.2$

M/2 solution in M/2 boric acid:

$k \times 10^6 = 45.3$

M/2 boric acid alone was 30.0×10^{-6}

Elevation of Conductivity = 8.1×10^{-6}

Conductivities of Erythritol.

Specimen from departmental museum: large crystals.

M/2 aqueous solution:

$k \times 10^6 = 25.0$

M/2 solution in M/2 boric acid:

$k \times 10^6 = 97.0$

M/2 boric acid alone was 30.0×10^{-6}

Elevation of Conductivity = 42.0×10^{-6}

Conductivities of 1:2-Propylene Glycol.

M/2 aqueous solution:

$k \times 10^6 = 16.2$

M/2 solution in M/2 boric acid:

$k \times 10^6 = 33.5$

Depression of Conductivity = 12.7×10^{-6}

Conductivities of Triethylene Glycol.

M/2 aqueous solution:

$k \times 10^6 = 7.6$

M/2 solution in M/2 boric acid:

$k \times 10^6 = 23.1$

Depression of Conductivity = 14.5×10^{-6}

Conductivities of Dulcitol.

Specimen from departmental museum.

M/2 aqueous solution:

$k \times 10^6 = 35.9$

M/2 solution in M/2 boric acid:

$k \times 10^6 = 660.0$

M/2 boric acid alone was 30.0×10^{-6}

Elevation of Conductivity = 594.1×10^{-6}

The dulcitol was somewhat slow in dissolving in water: it appeared to dissolve more rapidly in the boric acid solution.

Conductivities of Mannitol.

The mannitol was obtained from British Drug Houses Ltd., it was washed with absolute alcohol and dried in a vacuum.

M/2 aqueous solution:

$k \times 10^6 = 12.3$

M/2 solution in M/2 boric acid:

$k \times 10^6 = 667.3$

M/2 boric acid alone was 29.0×10^{-6}

Elevation of Conductivity = 626.0×10^{-6}

Preparation of γ-methylglucoside.

The methylglucofuranoside was prepared according to the method of Fischer[9], by the action of 1% methyl-alcoholic-HCl (400g.) on finely powdered α-glucose (20g.): the HCl solution and the glucose must be quite free from water. The glucose was completely dissolved on shaking for 5 hours: after standing a further 15 hours the liquid was neutralised with silver carbonate and evaporated to a syrup. The final stage of the evaporation was carried out in a bottle instead of a flask, in order to simplify the extraction with ethyl acetate: glass beads were added to the syrup, which was fairly strongly reducing to Fehling's solution, and extraction carried out by shaking 5 times/20 minutes with 200c.c. ethyl acetate at room temperature.

The extracts were somewhat turbid and were cleared by filtration through a fine-grain paper: the 1000c.c. of extract were then evaporated to about 200c.c. at which stage a considerable quantity of a white syrupy emulsion slightly reducing to Fehling's solution was present in the flask.

The remainder of the liquid was poured into another smaller flask, and all the ethyl acetate

removed: a thick yellowish, non-reducing syrup was obtained. This syrup distilled readily at 220°(bath)/ 0.04mm.. The distillate was still slightly yellow, but had no reducing action and was sufficiently pure for conductivity measurements.

OMe; Found, 15.8%; Calc. for $C_7H_{14}O_6$, 16.0%

$[\alpha]_D^{18°} = -14°$ (c = 5.0 in water)

Conductivities of methylglucofuranoside.

M/2 aqueous solution:

$k \times 10^6 = 15.0$

M/2 solution in M/2 boric acid:

$k \times 10^6 = 156.3$

M/2 boric acid alone was 30.0×10^{-6}

Elevation of Conductivity = 111.3×10^{-6} .

Preparation of γ-methylgalactoside.

The method followed was that of Haworth Ruell and Westgarth[10].

A 1% solution of galactose in 1% methyl-alcoholic-HCl was employed: after 24 hours, with intermittent shaking for 8 hours, all the galactose had dissolved. The solution at this stage gave $[\alpha]_D^{18^\circ}$ = (approx.) -56°, which was fairly close to Haworth's minimum value for the reaction namely, -58.1°. Silver carbonate was therefore added, and the filtrate from the neutralisation evaporated and extracted ten times/20mins. with 100c.c. portions of ethyl acetate at room temperature. The extracts were filtered through a fine-grain paper and the ethyl acetate completely removed by evaporation under reduced pressure.

A thick yellowish syrup was obtained, non-reducing to Fehling's solution.

$$[\alpha]_D^{18^\circ} = -57.6^\circ \ (c = 2.3 \text{ in water})$$

OMe; Found, 15.1%; Calc. for $C_7H_{14}O_6$, 16.0%

Several unsuccessful attempts to distil the syrup were made.

Comparison of the Rates of Hydrolysis of Normal and γ -Methylgalactosides in N/10 HCl.

In each case, the same weight of substance was made up to 25c.cs. in a flask with N/10 HCl; after dissolving completely at room temperature the solution was transferred to a flask, fitted with a reflux condenser, in a bath maintained at 90°C. Polarimeter readings were taken on the solutions from time to time.

Apart from the difference in the initial rotations, the tables show the marked difference in susceptibility of the two substances to N/10 HCl. In the case of the γ -methylgalactoside, which has a somewhat greater distance to travel to equilibrium, the latter was reached in approximately 5 hours. With the normal galactoside, the hydrolysis was only half-completed after 9 hours.

It was found that at room temperature, N/10 HCl had no effect on either substance, even after several hours.

Hydrolysis of α-methylgalactopyranoside:

Weight of crystals taken = 0.6020g.

Minutes	Corrected Polarimeter Reading	$[\alpha]_D^{20^\circ}$
15	4.22	+ 175.3°
30	4.14	171.9
60	4.07	169.0
120	3.87	160.7
200	3.69	153.2
240	3.60	149.5
320	3.40	141.2
400	3.19	132.5
540	2.89	+ 120.0°

Hydrolysis of γ-methylgalactoside.

Weight of syrup taken = 0.6020g.

Minutes	Corrected Polarimeter Reading	$[\alpha]_D^{20^\circ}$
10	0.85	-35.3°
20	0.28	-11.6
30	0.05	+ 2.1
45	0.52	21.6
60	0.97	40.3
75	1.27	52.8
100	1.45	60.3
240	1.74	$+72.3^\circ$
⋮	⋮	⋮

Conductivities of γ-methylgalactoside.

M/2 aqueous solution:

$$k \times 10^{6} = 30.0$$

M/2 solution in M/2 boric acid:

$$k \times 10^{6} = 48.0$$

M/2 boric acid alone was 30.0×10^{-6}

Depression of Conductivity = 12.0×10^{-6}

Preparation of α-methylmannofuranoside.

The method of Haworth, Hirst and Webb[11] was employed. 15g. of mannose were shaken with 300c.c. of 1% methyl-alcoholic-HCl. The mannose had all dissolved in less than one hour: after shaking a further two hours, the solution was allowed to stand for twenty hours and was then neutralised with silver carbonate. The procedure was then the same as for the γ-methylglucoside, except that the ethyl acetate extraction was carried out twelve times/20 minutes with 50c.c. portions of ethyl acetate. The extracts were filtered through a fine-grain paper and evaporated to remove all the solvent: as in all these experiments, the evaporation was carried out under reduced pressure and in a water-bath at not more than 45°C: a little dry methyl alcohol was added towards the end to assist the evaporation.

A thick syrup was obtained, very slightly yellow in colour, and non-reducing to Fehling's solution. The syrup crystallised out completely on nucleating with a crystal of the substance kindly provided by Professor W.N. Haworth F.R.S.

Conductivities of α-methylmannofuranoside.

The crystals, which had a yellowish tinge, were recrystallised from methyl alcohol-ether, using just sufficient methyl alcohol for solution. After the first recrystallisation, in which too much ether was added and the substance precipitated too rapidly, the conductivity of an M/2 aqueous solution was 53×10^{-6}. A further recrystallisation was carried out, yielding colourless, needle-shaped crystals.
m.p. 119°, $[\alpha]_D^{18°} = +113°$ (c = 1.5 in water)
A rotation was carried out in M/2 boric acid instead of water and gave $[\alpha]_D^{18°} = +112.2°$ (c=0.5 in M/2 H_3BO_3)

M/2 aqueous solution:

$k \times 10^6 = 20.0$

M/2 solution in M/2 boric acid:

$k \times 10^6 = 3400.0$

M/2 boric acid alone was 30.0×10^{-6}

Elevation of Conductivity = 3350.0×10^{-6}

Conductivities of β-d-fructose.

The fructose was supplied by British Drug Houses Ltd., its conductivity was found to be high, being about 120 x 10^{-6}; it was therefore purified by slow recrystallisation from absolute alcohol, followed by washing with acetone.

$[\alpha]_D^{18^\circ}$ = -130° (c = 3.6 in water)

M/2 aqueous solution:

k x 10^6 = 28.6

M/2 solution in M/2 boric acid:

k x 10^6 = 762.0

M/2 boric acid alone was 30 x 10^{-6}

Elevation of Conductivity = 703.4 x 10^{-6}

Conductivities of α-l-sorbose.

Specimen from departmental museum, large crystals.

m.p. 164-165°, $[\alpha]_D^{18^\circ}$ = -43.5° (c = 1.0 in water)

M/2 aqueous solution:

k x 10^6 = 24.8

M/2 solution in M/2 boric acid:

k x 10^6 = 2215.0

M/2 boric acid alone was 31 x 10^{-6}

Elevation of Conductivity = 2159.2 x 10^{-6}

Conductivities of α-l-sorbose (contd):-

M/10 aqueous solution:

$$k \times 10^6 = 9.3$$

M/10 solution in M/10 boric acid:

$$k \times 10^6 = 212.0$$

M/10 boric acid alone was 5.1×10^{-6}

Elevation of Conductivity $= 197.6 \times 10^{-6}$

This is in good agreement with the value of the elevation observed by Böeseken and Leefers[13] for an M/10 solution.

Bibliography.

1 Hudson & Dale.....J. Am. C.S. 1917 39 322

2 Behrend.....Ann. 1907 353 107

3 Bott, Haworth & Hirst....J.C.S. 1930 1395

4 Paterson & Robertson.....J.C.S. 1929 300

5 West & Holden.....J. Am. C.S. 1934 56 930

6 Haworth, Hirst & Webb....J.C.S. 1928 2681

7 Baird, Haworth & Hirst...J.C.S. 1935 1201

8 Hornel & Butler.....J.C.S. 1936 1361

9 Fischer.....Ber. 1914 47 1984

10 Haworth, Ruell &.....J.C.S. 1924 125 2468
Westgarth

11 Haworth, Hirst & Webb....J.C.S. 1930 658

12 Fischer.....Ber. 1894 27 673

13 Böeseken & Leefers.....Rec. Trav. chim.1935 54 865

14 Böeseken.....Rec. Trav. chim.1921 40 360

Part Three

D I S C U S S I O N

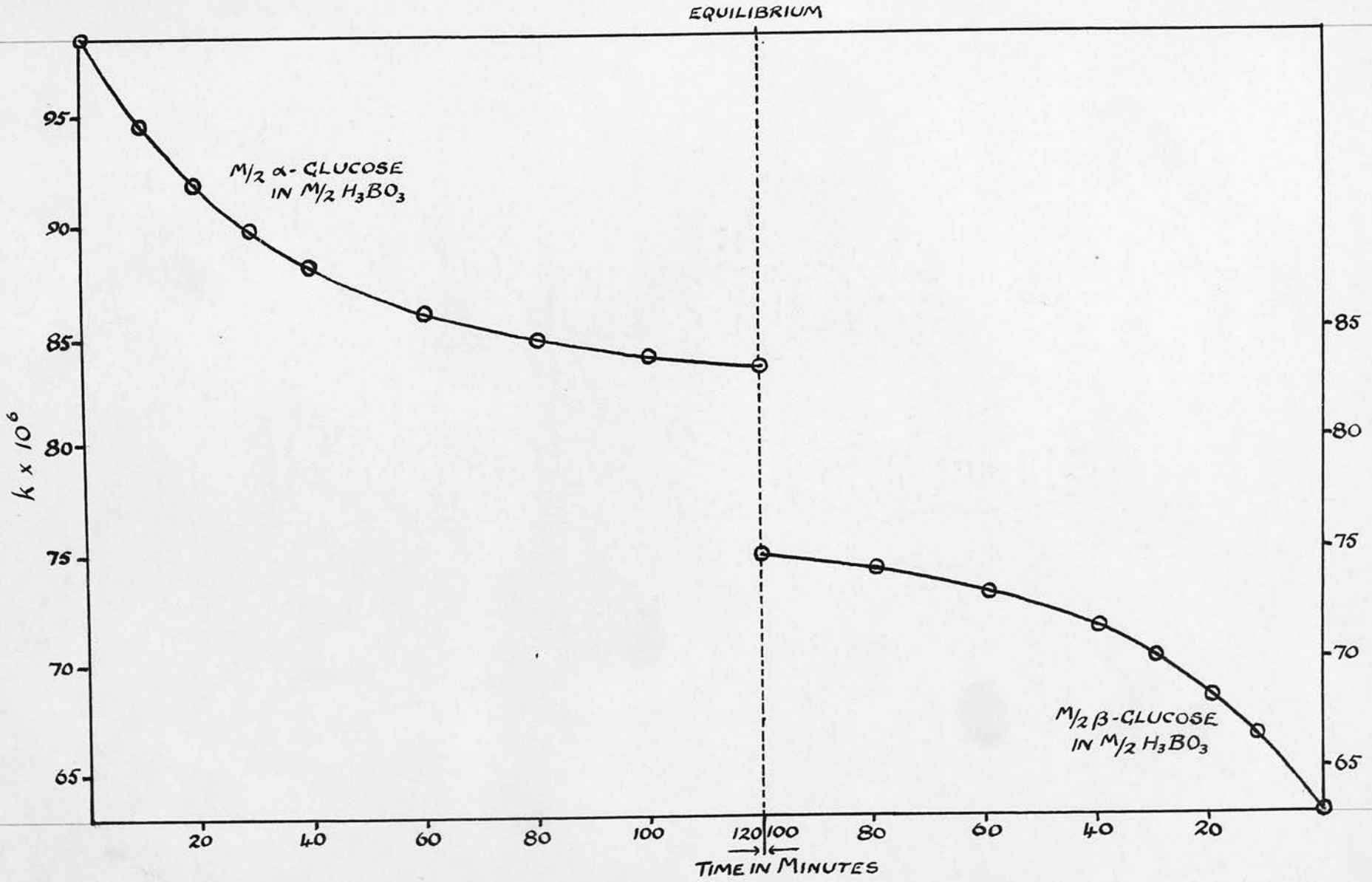
In 1913 Böeseken[1] carried out a series of experiments on the effect of glucose on the electrical conductivity of boric acid solutions. The results he obtained would appear at first sight to be somewhat peculiar: for example, he found that with α -d-glucose, the conductivity of a molar solution in M/2 boric acid fell from an initial value of 147 x 10^{-6} to a final value of 130 x 10^{-6}, whereas with the β -form in a similar solution, an initial value of about 105 x 10^{-6} rose to 122 x 10^{-6} at equilibrium. A fact to be noted from these figures, and which was remarked upon by Böeseken in his paper, is that the conductivity values of the two solutions at equilibrium are not identical as might be expected.

To confirm these results, and if possible to explain them, experiments were carried out with α- and β -d-glucose in aqueous and in boric acid solutions. As can be seen from the figures (pp.33-35), results were obtained very similar to those of Böeseken: the conductivity, in boric acid solution, of M/2 α -d-glucose fell from 98.5 x 10^{-6} to 83.3 x 10^{-6} whereas that of the β -form rose from 63.0 x 10^{-6} to 75.0 x 10^{-6}. Here again the equilibrium values are not coincident, but it must be remembered that the conductivity of M/2 aqueous α -form is 11.5 x 10^{-6}

whilst that of the β -form is 8.5×10^{-6}. We should therefore expect a difference of at least 3×10^{-6} in the equilibrium values; the fact that the difference is somewhat greater than this may possibly be explained by the addition of boric acid, in which solution the difference need not necessarily be the same as in aqueous solution. As Böeseken showed, the difference in the equilibrium values diminishes with the concentration.

The suggestion that this "gap" at equilibrium is due to the initial difference in the conductivities of the α- and β-glucoses in aqueous solution is borne out by the work of Verschuur[2], who carried out similar experiments: the specimens of α- and β-d-glucose which he employed possessed almost identical conductivities, namely α-form 5.34×10^{-6}, β-form 5.33×10^{-6}. He found that the equilibrium values of the conductivities in M/2 boric acid solution were also almost identical, 80.95×10^{-6} and 79.83×10^{-6} respectively, thus giving an almost continuous curve. Böesekens specimens had an initial difference in conductivity of about 2×10^{-6}.

From the curve, it can be seen that α-d-glucose has a considerably greater effect on the conductivity of boric acid solution than has β-d-glucose, the pure α-form giving an elevation of


EQUILIBRIUM
M/2 α-GLUCOSE IN M/2 H_3BO_3
M/2 β-GLUCOSE IN M/2 H_3BO_3
$k \times 10^6$
95
90
85
80
75
70
65
85
80
75
70
65
20
40
60
80
100
120
100
80
60
40
20
TIME IN MINUTES

59.4×10^{-6} and the pure β-form 26.5×10^{-6}. It is also to be noted that equilibrium is reached in a shorter time with β-glucose than with α-glucose, the former being practically at equilibrium in 100 minutes whilst the latter takes 120 minutes: this would be accounted for by the fact that an equilibrium glucose solution contains over 60% of the β-form, so that the latter will have a shorter distance to travel to equilibrium. From a further series of experiments it was seen (p.36) that the conductivity in each case had the same equilibrium value whether the boric acid solution was added at the beginning, or whether the glucose solutions were first allowed to come to optical equilibrium before the addition of the boric acid. It would therefore seem that if any reaction does take place between sugar and boric acid, it must be practically instantaneous.

The next substance examined was α-d-galactose, which gave an elevation of conductivity of 29.5×10^{-6}. Now, for accurate comparative work, it is obviously desirable that the conductivities, in aqueous solution, of the substances under examination should be as nearly as possible the same. The reason for this is that the observed elevation or depression of the conductivity of boric acid solution on the addition of a sugar or sugar derivative depends not only on the

nature of the substance, but also, though generally to a lesser extent, on the conductivity of the substance alone in aqueous solution. This effect was noted when dealing with the methylated glucoses: for example, tetramethyl glucose with a conductivity of 50.0×10^{-6} in M/2 aqueous solution gave a net depression of conductivity of M/2 boric acid solution amounting to 24.0×10^{-6}, whereas the same substance after further purification so that its aqueous conductivity was reduced to 7.0×10^{-6} caused a net depression of 14.1×10^{-6}. On several occasions e.g., with trimethyl methylglucoside, tetramethyl methylglucoside and trimethyl mannose, conductivity experiments were carried out on a specimen of comparatively high conductivity before purifying the substance further. From a comparison of the results it can be taken as a general rule that for any one substance, the higher its conductivity, that is to say, the more impure it is, then the greater will be the observed depression of conductivity, or, if the effect is positive, then the smaller will be the elevation.

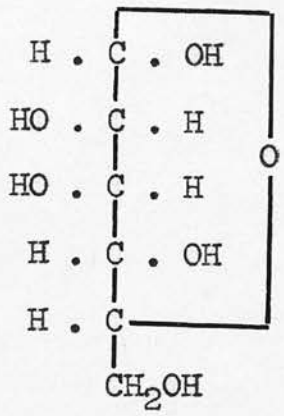
While in every case the conductivity of the substance under examination has been brought as low as possible, either by recrystallisation, washing or distillation in a high vacuum, it was often found to be a matter of great practical difficulty to reduce the

conductivities of some of the substances to figures comparable with those recorded for the α - and β - glucoses, the difficulty being aggravated , in some cases, by the limited quantities available. Although a great deal of time was spent in purifying compounds prepared and procured, one had often to be content with a comparatively high conductivity figure. This applied more to some of the free sugars supplied from various sources, and not so much to the compounds prepared in the laboratory, which were all of reasonably low conductivity, and in many cases of a higher degree of purity than the specimens quoted in the literature. Comparison of results and subsequent deductions were thereby rendered more difficult. This inconsistency in the conductivities of so-called non-electrolytes is to be seen in all the work on this subject, the substances used in some cases having values much too high to be of any real value.

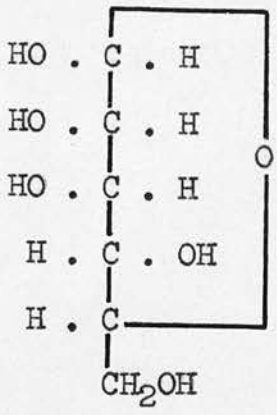
It can be assumed then that the observed increase in conductivity due to α-d-galactose would have been considerably enhanced had the initial conductivity of the galactose in aqueous solution been as low as that of glucose: it may be reckoned that the effective increase is of the same order in both cases, being slightly greater, if anything, with the glucose. Again, as with α-d-glucose, the conductivity of α-d-

galactose in boric acid solution falls as mutarotation proceeds: this indicates that the β-form in boric acid solution has a smaller conductivity than the α-form under the same conditions.

Similar results (p.42) were obtained with a specimen of d-mannose, the optical rotation of which showed it to be the β-form: the purest specimen available had the comparatively high conductivity, in M/2 aqueous solution, of 78×10^{-6}. Recrystallisation was not successful in reducing this value. As can be seen, the conductivity in boric acid solution showed but little elevation, but a considerable increase could be expected were the conductivity of the β-d-mannose as low as that of glucose. An interesting application of Böeseken's "boric acid test" for distinguishing cis- and trans-forms arises here: as can be seen from the figures (p.42), the conductivity of the mannose in boric acid fell with time to an equilibrium value. This fall was to be expected, according to Böeseken's theory, if the original mannose were the "cis"-form - in the case of d-mannose this would be synonymous with the β-form. (See diagrams on next page.) The results with α-l-rhamnose (p.43) are also to be expected on Böeseken's hypothesis, the conductivity of the α- or trans-form increasing on mutarotation.



α-d-mannose



β-d-mannose

As the rotation showed, the mannose was the β-form.

The next step was to investigate the conductivities of a number of methylated derivatives of the sugars, in order to discover whether the increase in the conductivity of a boric acid solution could be attributed to any one particular hydroxyl group in the sugar molecule, or whether two or more were required and if so, what positions they occupied. When every hydroxyl group was replaced as in tetramethyl methylglucoside, a considerable depression of conductivity of boric acid solution was observed (p.49): 2:3:6-trimethyl glucose and 2:3:4:6-tetramethyl glucose both show depressions, as also does 2:3:6-trimethyl methylglucoside (pp.51,48 and 50respectively). α-Methylglucoside and α-methylgalactoside both cause a slight depression of conductivity so that it is evident, when the considerable elevations due to glucose and galactose are considered, that the increase

in conductivity is in some way connected with the hydroxyl group attached to the first carbon atom. That the increase is not due entirely to this group, and indeed that this hydroxyl alone is ineffective, is shown by the depressions with the 2:3:6- and 2:3:4:6- derivatives. Again sucrose, which contains eight free hydroxyl groups, but in which the reducing group of the glucopyranose portion of the molecule is attached to the fructofuranose unit, gives no increase in conductivity (p.44)

Now according to Böeseken[3], before any increase in conductivity is observed, there must be a pair of cis-hydroxyl groups available on adjacent carbon atoms: this, taken in conjunction with the above results leads to the conclusion that it is the hydroxyl groups on the first and second carbon atoms which are responsible for the influence on boric acid solution. If the results with 3:4:6-trimethyl α-mannopyranose (p.54) are studied it will be observed that it shows a change in conductivity with time when in boric acid solution, and that it is the only one of the methylated derivatives under examination which does so. The initial depression of conductivity is seen to become less as mutarotation proceeds, so that an initial depression of 12.1×10^{-6} becomes a depression of 4.7×10^{-6} at equilibrium. Now the original

trimethyl mannose was the α- or "trans"-form whereas at equilibrium there is present a mixture of the α- and β- or "cis"-form: it is therefore reasonable to assume that the β-form exerts a positive influence on the conductivity of boric acid solution.

The fact that α-d-galactose, with an extra pair of cis-hydroxyl groups on carbon atoms 3: and 4: has no greater effect on the conductivity than α-d-glucose, and also that α-methylgalactoside with the same pair of hydroxyl groups available, has no positive influence, would appear to indicate that these groups have no part in increasing the conductivity. Again, the results with methylglucoside and methylgalactoside show that the hydroxyl groups on the other carbon atoms have little or no effect.

Generally speaking, therefore, it can be seen that Böeseken's "boric acid test" stating that an increase in conductivity is observed with the cis-form of a hydroxy-compound and no increase with the trans-form applies to the sugars mentioned above, in particular to 3:4:6-trimethyl mannopyranose in which there is no possibility of compound formation with boric acid other than at carbon atoms 1: and 2:, a restriction not imposed on the studies on free glucose, galactose and mannose. Where it cannot always be said

definitely that the trans-form has no effect, as witness the results with β-d-glucose, it is at least evident that the cis-form has a markedly stronger positive influence than the trans-form. The positive result with β-glucose could conceivably be explained on the assumption that when glucose is dissolved in water some of it exists as a straight-chain form, for, as will be seen later, the amount of such a straight-chain polyhydroxy compound necessary to cause a slight rise in conductivity would be very small, e.g.,sorbitol (p.100), dulcitol (p.64), glucose diethyl mercaptal (p.61).

At first sight there appears to be no reason why cis-hydroxyl groups on carbon atoms 1: and 2: should be responsible for an increase in the conductivity of boric acid solution, whilst cis-hydroxyl groups on 3: and 4:, as in galactose and methylgalactoside, should have no effect. Both pairs being cis-, they would be expected to have a similar effect. A possible explanation of this fact, based on the configuration of the hexatomic ring can, however, be put forward. A homocyclic pentatomic ring is practically strainless when perfectly flat; a six-membered ring, however, such as is present in the pyranose sugars can no longer be quite flat without

inducing excessive strains in the linkages. To obtain a perfectly strainless ring, the carbon atom opposite the oxygen atom, that is the third carbon, may occupy one of two alternative positions according to the Sachse-Mohr hypothesis. Number 3: carbon atom may be "sticking up" on the same side of the ring as the oxygen atom or on the opposite side: the former possibility gives rise to the so-called "bed" form of Sachse ring (Fig.1), the latter the "chair" form (Fig.2)

Fig. 1

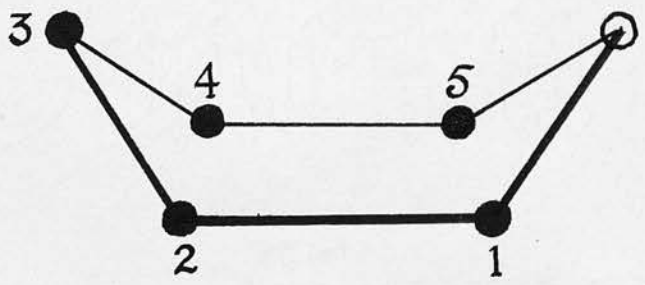
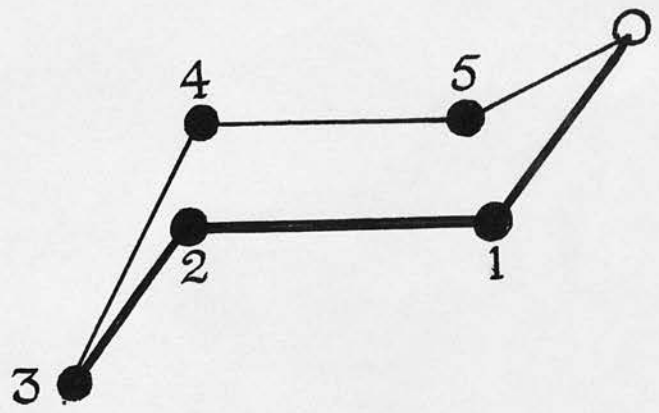
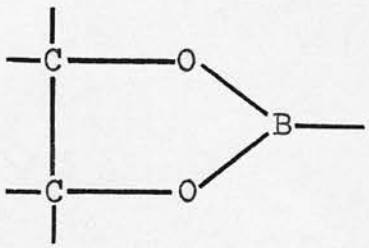


Fig. 2



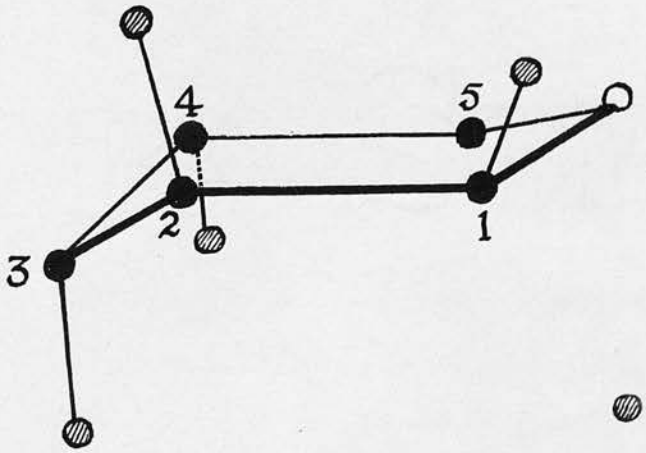
Models of pyranose rings were constructed having cis-hydroxyl groups on carbon atoms 1: and 2: and on 3: and 4: representing α-d-glucose and α-d-galactose respectively. Now if the oxygen atom is

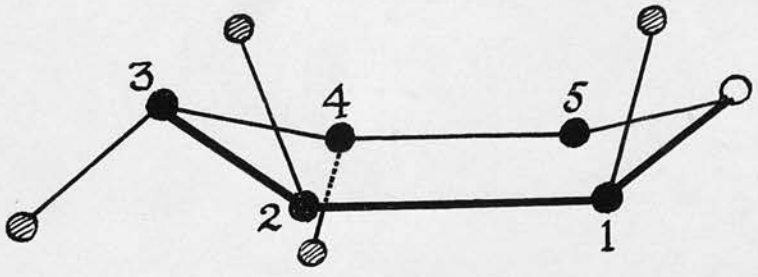
projecting a short distance, as cannot be doubted[4], then the C-OH linkages from carbon atoms 1: and 2: are thrown out of plane with one another. On Böeseken's hypothesis no complex formation and therefore no increase in conductivity will occur unless they are in plane, so that the pentatomic ring of the boron complex



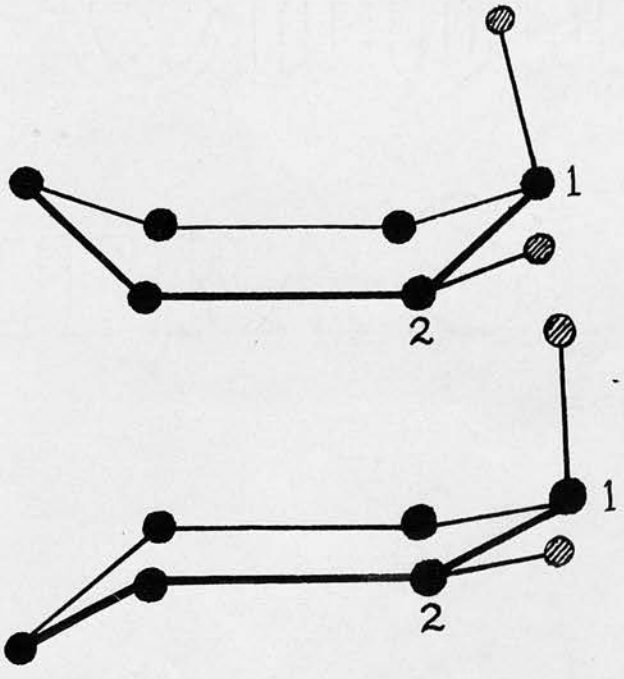
may be formed without strain. Again, the remainder of the ring is still under considerable strain, with two of the angles very considerably outside the allowable deviation from the tetrahedral angle. To relieve this strain number 3: carbon atom may be moved so as to yield one or other of the Sachse forms: if the ring is put into the "chair" form it can be seen from a model that not only are the cis-hydroxyl groups on carbon atoms 1: and 2: out of plane, but every hydroxyl group attached to the carbon atoms of the ring is out of plane with any hydroxyl group on the adjacent atoms. That is, assuming we have cis-hydroxyl groups on adjacent carbon atoms, they cannot have, if we follow Böeseken's theory, any positive influence on the conductivity no matter to what pair of carbon atoms

they are attached; neither the positive influence of α -d-glucose, nor the failure of α -d-galactose to have any greater effect, nor the depression due to methylgalactoside could thus be accounted for. All these facts can, however, be explained if we assume that the pyranose ring exists in the "bed" form. Examination of a model shows that the cis-hydroxyl groups on carbon atoms 1: and 2: are now in plane, whereas those on atoms 3: and 4: are out of plane. Thus the latter pair of hydroxyl groups would not be expected to have any positive influence on the conductivity of boric acid solution.





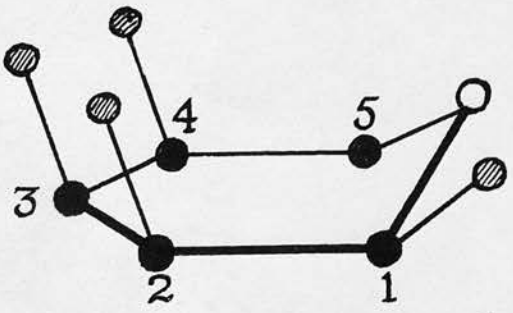
Cis-cyclohexane 1:2-diol and cis-cyclopentane 1:2-diol provide interesting examples of the relation of ring-configuration to the effect of the compound on the conductivity of boric acid solution. The latter substance has, of course, a planar ring, the cis-hydroxyl groups being therefore situated so that a pentatomic ring containing boron may be formed without strain. If the cyclohexane diol takes up one of the strainless Sachse forms one would expect the hydroxyl groups to be out of plane.



This would also explain why the cyclic acetals of inositol and quercitol cannot be prepared[5]. This ring formation for the cyclohexane diol is also borne out by the conductivity measurements of Böeseken[6] who

finds a marked elevation (150 x 10^{-6}) with the cyclopentane diol but a depression of conductivity with cyclohexane diol: this would indicate the cis-hydroxyl groups to be out of plane in the hexatomic ring.

It must be admitted that strong objections to the supposition that the pyranose sugars exist in one or other of the strainless Sachse ring-forms have been raised by E.Gordon Cox and his co-workers[7] as a result of their fundamental researches using X-rays. "This view" according to Cox " involves various assumptions, chief of which are that the different radius and (possibly) different valency angle of the oxygen atom can be ignored and that the carbon valencies are strained unless they are directed to the corners of a regular tetrahedron". Cox postulates a "flat" ring for the pyranose sugars and glucosides he has examined, in which the five carbon atoms are nearly but not necessarily exactly co-planar, the oxygen atom being displaced out of this plane by $\frac{1}{2}$-1 Å



As a result, cis-hydroxyl groups at carbon atoms 2: and 3: and at 3: and 4: are nearly co-planar, whereas those at 1: and 2: are considerably out of plane.

It is apparent therefore, that the configuration of the pyranose ring proposed by Cox and his co-workers will not explain the results of the conductivity experiments, provided that the complex formation theory of Böeseken is correct and that the enhanced conductivity is due to the formation of a strainless pentatomic ring containing boron. As pointed out above, the conductivity results obtained would require the cis-hydroxyl groups on carbon atoms 1: and 2: to be in plane and those at 3: and 4: out of plane. There would appear to be, in solution, some possibility of divergence from the "flat" ring especially in the case of galactose, since 1:2,3:4-diacetone galactose is formed with ease by the direct condensation of acetone and galactose in the presence of sulphuric acid. Furthermore, the well-known reactivity of the hydroxyl group attached to the first carbon atom in α-d-galactose – the potential reducing group – may assist the formation of a 1:2-cis-hydroxy boric acid complex, and once such a complex is formed, and the cis-hydroxyl groups on carbon atoms 1: and 2: are in one plane, it follows that if the pyranose ring is to be strainless, the hydroxyl groups on carbon atoms 3: and 4: will be unfavourably placed for complex formation with the boric acid. This latter consider-

ation, however, would not explain the result obtained with α-methylgalactopyranoside, which gives a depression of conductivity, so that unless some form intermediate between the Sachse "bed" form and the "flat" ring proposed by Cox can be considered to exist, it appears difficult to interpret the results.

Continuing the examination of the conductivity results, the case of tetramethylglucose is important: it was upon his results with this substance that Irvine[8], as already stated, based a theory of mutarotation. Since Böeseken and Couvert[9] obtained results in entire disagreement with those of Irvine, thus completely upsetting this theory, it is interesting to compare the results obtained in this research with these earlier conflicting results. The specimen of tetramethyl glucose prepared for this experiment was of a high degree of purity having a conductivity of only 7×10^{-6} in M/2 aqueous solution, whilst that used by Böeseken and by Irvine had a corresponding value of almost 50×10^{-6}. The results obtained agree fairly well with those of Böeseken, and no huge increase of conductivity, as found by Irvine, was observed: the fact that the depression noted was somewhat less than that of Böeseken, was probably due, as previously suggested (p.80) to the greater

conductivity in aqueous solution of the specimen employed by that author. Irvine actually obtained an initial depression comparable to that of Böeseken, but the conductivity rose very rapidly: this may have been due to faults in the electrodes of the cell or in the circuit used (cf. Glasstone, "Electrochemistry of Solutions", 1930 pp.59-60); as mentioned previously (p. 25) trouble was experienced in this research when the use of platinised electrodes was attempted. Irvine and Steele[8] based their objections to Böeseken's theory of increased conductivity on their results with tetramethyl glucose and tetramethyl methylglucoside: they found a marked increase in the conductivity of boric acid solution when either of these substances was present, so they disagreed with the necessity for having a pair of cis-hydroxyl groups before any increase in conductivity could be expected. Böeseken and Couvert[9], however, found only a marked depression of conductivity in the presence of tetramethyl methyl-glucoside and this result is borne out by the values obtained in this research (p.49) a depression of 18×10^{-6} being observed.

Results of Viscosity Experiments.

The viscosity experiments on glucose and the methylated glucoses were undertaken in order to see whether any relationship could be found between viscosity values in aqueous and boric acid solution and conductivity results in corresponding solutions. Actually no such direct relationship was discovered, but this was not surprising since viscosity changes for any one substance will be very small as compared with the corresponding conductivity change. A relation however, can be traced between the volume of the dissolved phase and the viscosity of the solution. The simple sugars provide examples of more or less spherical molecules, and for such substances Einstein[10] arrived at a relationship between the viscosity and the concentration. This may be written in modified form as

$$\eta_{sp} \cdot S/c = K$$

Where η_{sp} is the specific viscosity of the solution, S the density of the dissolved phase and c its weight-concentration. S/c is thus an expression of the volume of dissolved phase. K is a constant for one class of substance.

In this research, the viscosities were all calculated as relative viscosities, water being taken as standard for the aqueous solutions with a viscosity = 1.00. For the boric acid solutions,

M/2 boric acid solution was the standard with a value of 1.05 (see tables, pp.59,60). The value for the specific viscosity is obtained by subtracting 1 from the value of the relative viscosity; S, the density of the dissolved phase, is calculated as shown below. The factor $\eta_{sp} \cdot S/c$ was then worked out for each substance in aqueous and boric acid solution, all solutions being M/2 as for the conductivity experiments. Good constancy of the value of this factor was obtained, as can be seen from the tables below, the constant varying only from .046 to .048 for aqueous and from .042 to .045 for boric acid solutions.

Example of density calculation:- (α-methylglucopyranoside)

Weight of 1c.c. water (from pipette) = 1.001g.

Volume of this at 18°C. = 1.003c.c.

Weight of glucoside taken = 0.097g.

∴ Weight of solution = 1.098g.

Volume of solution = 1.098 x 9445/967c.c.

= 1.073c.c.

Volume of glucoside (in solution) = (1.073-1.003)c.c.

= 0.070c.c.

∴ Density = 097/.070

= 1.386

Comparison of Viscosity with Volume of Dissolved Phase.

M/2 aqueous solutions

Dissolved Phase	η_{sp}	c	η_{sp}/c	S	$\eta_{sp} \cdot \frac{S}{c}$
α-d-glucose	.250	8.25	.0303	1.552	.046
β-d-glucose	.250	8.25	.0303	1.552	.046
α-methylgluco-pyranoside	.295	8.82	.0335	1.386	.046
3:4:6-trimethyl α-mannopyranose	.360	9.98	.0361	1.337	.048
2:3:6-trimethyl methyl-glucopyranoside	.400	10.55	.0379	1.242	.047
2:3:4:6-tetramethyl glucose	.390	10.55	.0370	1.242	.046
2:3:4:6-tetramethyl methylglucoside	.420	11.10	.0378	1.275	.048

η_{sp} = Specific viscosity

c = Weight-concn. of dissolved phase

S = Density of dissolved phase, by calculation

M/2 solutions in M/2 boric acid:

Dissolved Phase	η_{sp}	C	η_{sp}/C	S	$\eta_{sp}.\frac{S}{C}$
α-d-glucose	.240	8.21	.0292	1.428	.042
β-d-glucose	.245	8.21	.0298	1.451	.043
α-methylgluco-pyranoside	.290	8.80	.0330	1.311	.043
3:4:6-trimethyl α-mannopyranose	.350	9.94	.0352	1.247	.044
2:3:6-trimethyl methyl-glucopyranoside	.400	10.50	.0381	1.166	.044
2:3:4:6-tetramethyl glucose	.390	10.50	.0372	1.180	.044
2:3:4:6-tetramethyl methylglucoside	.415	11.10	.0374	1.202	.045

It will be noted that the relative viscosity increases with increase in molecular weight; this is analogous to the increasing depression of conductivity on the introduction of an increasing number of methoxyl groups, and both these facts are complementary to the above relation between viscosity and molecular volume.

The next class of substance to be examined was that of open-chain hydroxy-compounds. Böeseken[11] found that ethylene glycol gave a slight depression of conductivity of boric acid solution: now this glycol has two adjacent hydroxyl groups, and since there is no increase in conductivity, Böeseken concluded that it must be the trans-form. The open-chain substances examined in this research were, in addition to glycol, glycerol, erythritol, dulcitol, mannitol, 1:2-propylene glycol, triethylene glycol and glucose diethyl mercaptal. From the results it is seen that no considerable increase in the conductivity of boric acid solution is encountered until we have more than three hydroxyl groups present; glycerol, it is true, gives rise to an increase, but this is very small, namely 8.1×10^{-6}. With erythritol, which has four hydroxyl groups, an increase of 42.0×10^{-6}

is observed. Penta-erythritol, which also possesses four hydroxyl groups, though coming into the same category as erythritol, was found by Böeseken[12] to cause a big increase in conductivity, namely 231 x 10^{-6}. Dulcitol and mannitol gave elevations of conductivity of 594 and 626 x 10^{-6} respectively. Böeseken[13] found that sorbitol gave an elevation of 794 x 10^{-6}.

The case of glucose diethyl mercaptal is important: being an open-chain compound with five free and adjacent hydroxyl groups a big elevation of conductivity is to be expected: this is actually the case, an M/10 solution effecting a net increase of conductivity of M/10 boric acid solution amounting to 176.2 x 10^{-6}. M/10 solution was employed in this case because of the low solubility of the mercaptal in water. Now, when we take glucose and substitute the first hydroxyl group by an indifferent group, leaving the pyranose ring intact, as for example in α-methylglucopyranoside, we evidently have a very different state of affairs, since the methylglucopyranoside gives rise not to a big increase, but to a slight decrease in the conductivity of boric acid solution. These two substances illustrate the fundamental difference in the properties of groups linked to the carbon atoms of a chain and to those of

a ring. In the case of the hydroxyl groups attached to the carbon atoms of a pyranose ring, very little movement is permitted and the groups appear to be fixed in relation to one another. In an open-chain compound, there is much greater freedom of movement, and there are numerous possibilities as to the respective positions of the hydroxyl groups: in a substance such as mannitol we may have, as can be seen by reference to a model, several possible pairs of hydroxyl groups in a favourable position for the formation of complexes with boric acid, through a pentatomic or hexatomic ring. There is also the possibility of the substance bending round into the form of a ring with one side open: there could then exist co-planar cis-(C-OH) linkages. Whatever form the open-chain compound takes up, there is a greater possibility of hydroxyl groups being favourably situated for effecting an increase in conductivity than there is in a ring-compound, and the possibility will increase with the number of hydroxyl groups present.

Compounds with furanose rings were the next to be examined. The initial purpose of this was to see whether the -CHOH.CH_2OH had any marked effect on the conductivity. The first substance to be

examined was methylglucofuranoside: it was found to give an elevation in conductivity of 110.3 x 10^{-6} in M/2 boric acid solution. This immediately impressed itself as a possible means of differentiating between the normal and the γ-form of the glucoside, since the former gave rise to a depression of conductivity. The results with methylgalactofuranoside, however, soon dispelled this belief, for this substance caused a depression of 12 x 10^{-6} in the conductivity of boric acid solution; finally crystalline α-methylmanno-furanoside, gave rise to an enormous increase of conductivity, namely 3350 x 10^{-6}.

So varied, and to some extent unexpected were these three results that the experiments were repeated and the authenticity of the compounds carefully checked, more especially in the case of the galactoside and the mannoside.

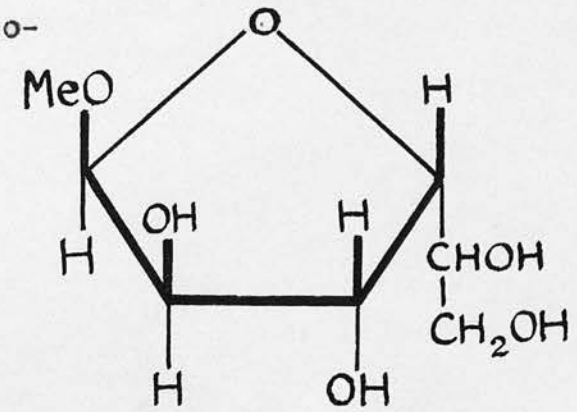
From the results there is one obvious conclusion – that the -CHOH.CH_2OH group alone has no positive influence on the conductivity since the methylgalactofuranoside contains this group. By comparison with ethylene glycol this is perhaps only to be expected, since the -CHOH.CH_2OH being a side-chain, permits complete freedom as to the relative positions of the hydroxyl groups, which will naturally incline to repel one another and hence become unfavourably

placed for complex formation with boric acid. What is more difficult to understand is the great difference in the effects of the three furanosides on the conductivity of boric acid solution. The projection formulae do not help much: the only difference to be noted there, is that the γ -mannoside possesses one pair of cis-hydroxyl groups (in addition to the $-CHOH.CH_2OH$) whereas the glucoside and galactoside have no cis-hydroxyls. Reference to the perspective formulae, however, or better still to models of the compounds, offers a possible explanation. Examination of the formulae below reveals the fact that the glucofuranoside has a hydroxyl group in close proximity to the $-CHOH.CH_2OH$ giving three hydroxyls within reasonable distance of one another and hence greater chance of the groups being favourably placed. In the case of the mannofuranoside, we have a pair of hydroxyl groups within easy reach of the hydroxyls in $-CHOH.CH_2OH$ and on the same side of the ring plane. We thus have four hydroxyl groups as in erythritol, but in the mannofuranoside they have very much less freedom of movement, hence the chances of complex formation are considerably enhanced. It can be seen too, more easily from a model, that if the side-chain is turned into a suitable position, a boron atom placed so to speak in the "middle" of the hydroxyl

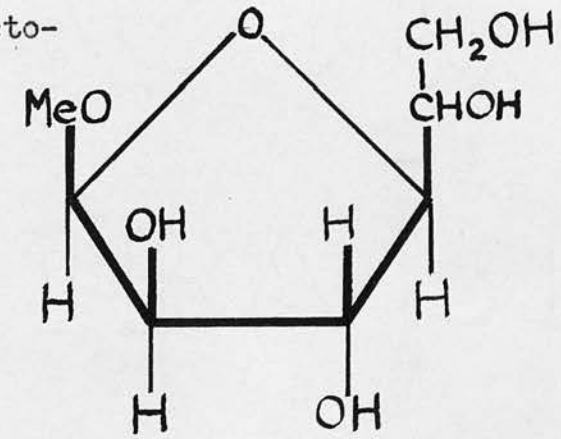
groups, could exist at the centre of a tetrahedron with these four hydroxyl groups at the corners.

Formulae of the methylglycofuranosides:-

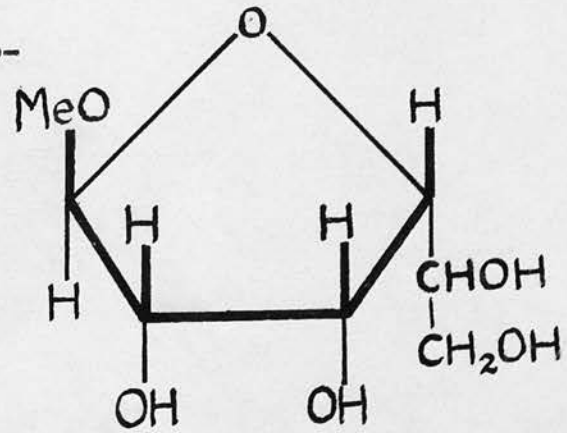
α-methylgluco-furanoside



α-methylgalacto-furanoside

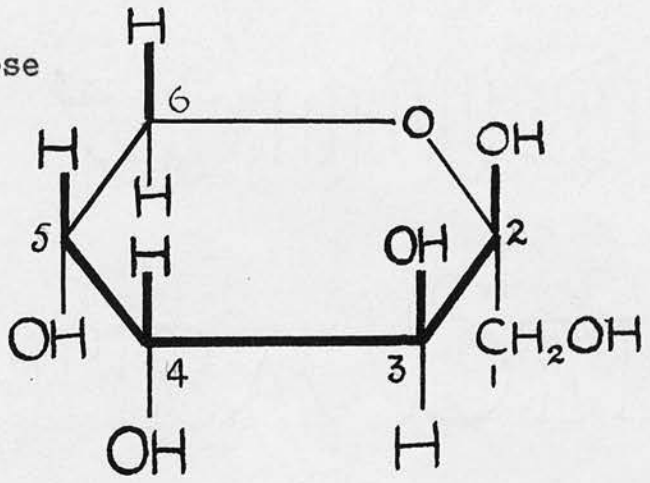


α-methylmanno-furanoside

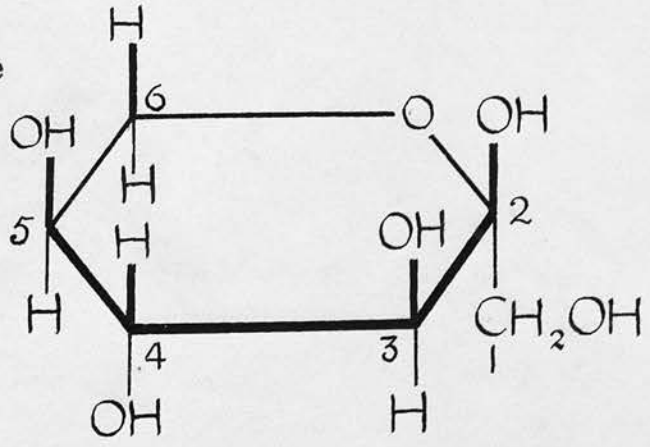


The results obtained with β -d-fructose and α -l-sorbose are interesting, since on the basis of the generally accepted formulae, the huge effect of the latter on the conductivity of boric acid solution is anomalous. As is recorded (p.74), the elevation due to β -d-fructose is 703.4×10^{-6}, that due to α -l-sorbose is 2159.2×10^{-6}. An examination of the perspective formulae shows that the fructose has cis-hydroxyl groups on C_4 and C_5, and in addition, the hydroxyl on C_3 is cis- to that on C_2.

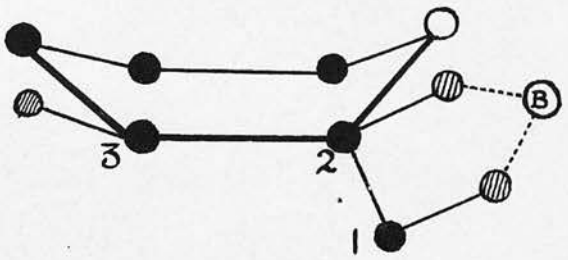
β -d-fructose



α -l-sorbose



It can also be seen from a strainless model of the ring, whether a Sachse or a "flat" form, that the hydroxyl on C_1 when turned towards that on C_2 can come into a position favourable for the formation, without strain, of a pentatomic ring with boric acid thus



From the formulae, exactly the same conditions would appear to obtain in sorbose at C_1 C_2 and C_3: the hydroxyl groups on C_4 and C_5 are, however, trans- with respect to one another. How then can the very much greater effect of sorbose on the conductivity of boric acid solution be explained? Fructose would appear to be the more likely to have the greater effect, since it possesses the additional cis-hydroxyl groups on C_4 and C_5, although as was pointed out previously (p.85), the corresponding cis-hydroxyl groups in galactose and methylgalactoside had no effect on the conductivity of boric acid solution.

If the formulae given above (previous page) are assumed to be correct, there would seem to be no possible explanation of the results; if both are normal

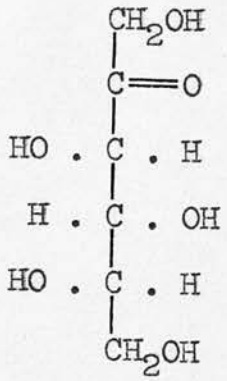
pyranose rings, the difference in effect would have to be accounted for on the different orientation of the hydroxyl groups round C_1 C_2 and C_3, those in sorbose being in some way more favourably disposed. Because of the similarity of the two formulae, however, it seems improbable that there can be any real difference here.

From the enormous elevation of conductivity due to α-l-sorbose, which can only be compared with that of α-methylmannofuranoside among the substances examined, one is led to the conclusion that there must be some fundamental difference in the configurations of the two molecules.

Some workers, e.g. Bosshard and Reichstein[14] write l-sorbose in the straight-chain form. It is possible that, in solution, it exists mainly as the ketonic straight-chain form (A), although there seems to be no reason why it should then have any greater effect on the conductivity than, for example, sorbitol. The suggestion can be made, however, that the sorbose, in solution, is in the form of a hydrated ketone (B), thereby having 7 available hydroxyl groups.

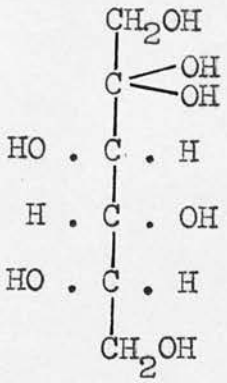
(See next page for formulae (A) and (B))

(A)



-l-sorbose

(B)



hydrated form

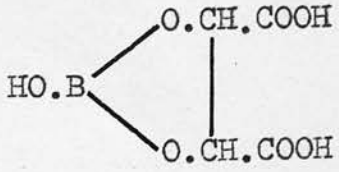
A similar explanation has been advanced by Böeseken[15] to account for the elevation of conductivity effected by pyruvic acid.

Rotation experiments have, in a few cases, been carried out in both aqueous and boric acid solutions. The substances of which the specific rotations were observed were all cyclic compounds namely α-d-glucose, β-d-glucose, 3:4:6-trimethyl α-mannopyranose and α-methylmannofuranoside. The effect of boric acid on the optical rotation of such straight-chain hydroxy-compounds as mannitol and sorbitol is well known, the addition of a substance such as boric acid being the best way of demonstrating optical activity in these substances. Thus, as already mentioned, Irvine[16] finds mannitol to have a negligible rotation in aqueous solution, whereas in M/2 boric

acid solution it has a specific rotation of + 28.3°. Addition of boric acid to solutions of active tartaric and malic acid produces marked changes in rotation[17].

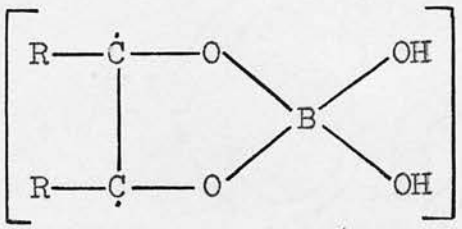
In the experiments carried out in this research no differences in the equilibrium values of the rotations were observed in aqueous and in boric acid solution, nor, as witness α - and β-d-glucoses was the velocity of the mutarotation affected. Tang and Sung[18] found that using 5.55M glucose solutions, the value for $[\alpha]_D$ had a sharp minimum equilibrium value of +46.6° in M/7.5 boric acid solution, whilst with greater or less amonnts of boric acid, the specific rotation $[\alpha]_D$ approached the value of +52.5° found for pure glucose solutions.

It is to be noted that whereas the optical rotation of open-chain substances is markedly altered by the presence of boric acid that of the cyclic substances examined undergoes no noticeable change at least at the concentrations studied. It is well known that the formation of a ring will enhance the optical rotatory power, so that in the open-chain compounds, such ring-formation may be the cause of the increase; Lowry[19] and others have for example tentatively advanced the structure



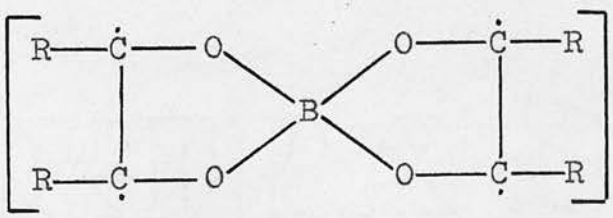
for borotartaric acid.

It has been mentioned on several occasions that there is considerable doubt as to whether on not the conductivity effects are dependent on the formation of complexes of boric acid and hydroxy-compound. Böeseken and his co-workers assume the formation of complexes which are more highly dissociated than boric acid itself, thus giving rise to an increase of conductivity. These dissociable complexes may possess some such structures as suggested by Hermans[24] and by Böeseken and Vermaas[25].



(1)

or



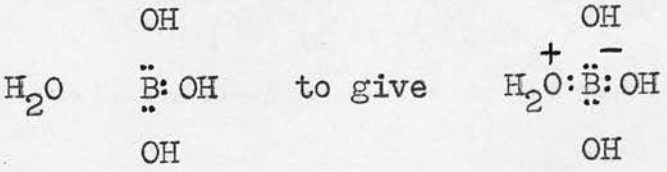
(2)

according as one or two molecules of the hydroxy-compound are involved, with the boron atom at the centre of a spiro-compound. Such structures are permissible since boron, by virtue of its position in the periodic table, and according to Pauling[20] by consideration of ionic radii, can be quadricovalent. The complex borotungstates, once thought to show boron capable of having a covalency of 6 have been shown to

possess a boron atom surrounded by four oxygen atoms being therefore 4-covalent. In aqueous solution it does not seem reasonable, especially since no solid complexes have ever been isolated from such solution, to suppose that there is a loss of water between the boric acid and particular hydroxyl groups of the organic molecules. It seems much more likely that the cyclic structure containing the boron atom is formed by some coordination process comparable to chelation, and that no actual anhydride formation takes place.

It has been shown that increase of conductivity is accompanied by increased hydrogen ion concentration[21]: it is therefore necessary to explain how this arises. A tentative theory may be proposed:-

Firstly, boric acid may react with water thus



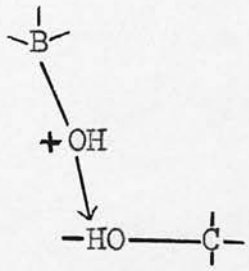
[cf. the stable compound NH_3BF_3, which is formulated similarly.]

this may be represented as $\overset{+}{H}\cdot\left[\overset{-}{B(OH)_4}\right]$ which on account of the charges, will be a weak acid.

Secondly, we may imagine the formation of semipolar double bonds or coordinate links from the

O atoms of $B(OH)_4$ to the hydroxyl hydrogen atoms of the organic molecule.

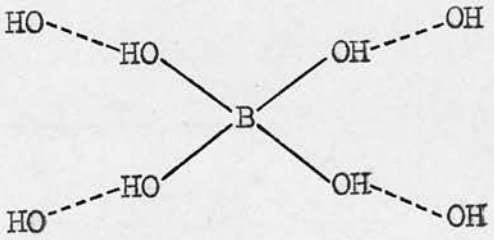
thus



The OH of the boric acid portion will thus become more positively charged, so that the negative charge on $\bar{B}(OH)_4$ is decreased: the weak acid $H.\left[B(OH)_4\right]$ will therefore tend to become progressively more strongly dissociated according to the number of hydroxyl groups concerned, so that there will be a corresponding increase in the hydrogen ion concentration. Accordingly, the greater the number of hydroxyl groups (up to 4) in a favourable position for the acceptance of an electron, the greater will be the tendency for the $H.\left[B(OH)_4\right]$ to dissociate, and hence the greater will be the increase in conductivity.

Precisely in what manner the increase in hydrogen ion concentration is brought about is difficult to say. There are other possible ways in which the oxygen atoms attached to the boron may become more positively charged, e.g. through a "hydroxyl bond"[22]. This would be more acceptable in

the light of modern theory which considers the coordination of hydrogen to be brought about by a resonance effect in which the hydrogen atom still links the two components; the resulting complex cannot be represented by a single structural formula but by two structures in which the hydrogen is covalently attached to first one and then the other of the combining residues. As has been suggested[23], however, until more is known about the coordination of hydrogen, it may be preferable, for complicated systems like the one under discussion, to represent such structures by a single formula in which the union is shown as a dotted line after the method of Alfred Werner, e.g.,



SUMMARY.

(1) As has been stated, the purpose of this research was to study the effects of hydroxy-compounds, more especially the simple sugars and their derivatives, on the conductivity of boric acid solution. An attempt has been made to correlate these results with the number and position of the hydroxyl groups present and thereby also to gain some insight into the structure of the molecule as a whole.

(2) It is generally assumed that the increased conductivity of boric acid solution on the addition of certain hydroxy-compounds is due primarily to the formation, in solution, of cyclic complexes between the hydroxy-compound and boric acid. According to Böeseken and his co-workers, who have advanced a great deal of experimental evidence in support of this theory, such complex formation will only take place, when adjacent cis-hydroxyl groups, in the same plane as the carbon atoms to which they are attached, are available. These complexes are supposed to be dissociable to a greater extent than the boric acid itself, the varying degrees of dissociation giving rise to corresponding increases in hydrogen ion concentration and hence also in conductivity. Using

this hypothesis of complex formation, several conclusions have been reached from a consideration of the experimental results:-

(a) With the pyranose sugars and their methylated derivatives:-

The only hydroxyl groups having any positive effect on the conductivity of a boric acid solution are those on C_1 and C_2

No increase in conductivity is observed unless both these hydroxyl groups are unsubstituted and are in the cis-position to one another.

(b) Using 3:4:6-trimethyl α-mannopyranose, the configuration is shown to be <u>trans</u>- with respect to the hydroxyl groups on C_1 and C_2, in contradistinction to the results of Böeseken and Couvert for β-mannose. This result was confirmed for β-mannose itself.

(c) The results for glucose, galactose and mannose (and their derivatives) appear to be best explained by the view that they possess the configuration either of the "bed" form of Sachse ring or something intermediate between this and the "flat" form proposed by Cox.

(d) With open-chain polyhydroxy compounds:-

No notable elevation of the conductivity of boric acid solutions is observed until the

molecule possesses more than three hydroxyl groups.

The elevation of conductivity increases with the number of hydroxyl groups.

(e) In the case of methylglycofuranosides, the ring being flat, the question of ring-configuration does not arise, the important factor being the orientation of the hydroxyl groups. Increase in conductivity appears to depend on the number of hydroxyl groups in proximity to one another. The group $-CHOH.CH_2OH$ by itself appears to have no positive effect on the conductivity.

(f) Sorbose brings about a very much greater increase of conductivity of boric acid solution than does fructose: this cannot be explained on the basis of the generally accepted pyranose structures for the two compounds, and a hydrated form of the ketonic formula is suggested for sorbose in solution.

(3) Examination of the viscosities of glucose and the methylated glucoses in aqueous and in boric acid solutions revealed no direct relationship between viscosity and conductivity, but in all cases very close agreement to the law that viscosity is a function of the volume of the dissolved phase was obtained.

In conclusion, the author wishes to thank Dr. E.G.V. Percival for his unfailing interest and his helpful suggestions and advice during the course of this research.

Bibliography.

1 Böeseken.....Ber. 1913 46 2612

2 Verschuur.....Rec. Trav. chim.1928 47 423

3 Böeseken.....ibid. 1915 34 96

4 Cox, Goodwin & Wagstaff..J.C.S. 1932 138

5 Karrer.....Helv.Chim.Acta. 1926 9 116

Micheel, Ruhkopf&Suckfüll.Ber 1935 68 1525

6 Böeseken.....Rec. Trav. chim.1921 40 558

van Loon.....Thesis, Delft 1919

7 Cox, Goodwin & Wagstaff..J.C.S. 1935 1495

8 Irvine & Steele.....ibid. 1915 107 1221

9 Böeseken & Couvert.....Rec. Trav. chim.1921 40 354

10 Einstein.....Ann. d. Physik. 1906 19 289

Staudinger & Heuer.....Ber. 1930 63 222

11 Böeseken & van Rossem....Rec. Trav. chim.1911 30 392

Böeseken.....Ber. 1913 46 2612

12 Böeseken.....Rec. Trav. chim.1921 40 553

Ber. 1913 46 2612

13 Böeseken.....cf. no. 12

14 Bösshard & Reichstein....Helv.Chim.Acta. 1935 18 959

15 Böeseken, Hansen.....Rec. Trav. chim.1915 35 309

& Bertram

16 Irvine & Steele.....cf. no. 8

17 Darmois.....J.Chim.phys. 1926 23 130,649

ibid. 1930 27 179

18 Tang & Sung.....Nature 1936 137 275

19 Lowry.....J.C.S. 1929 2853

20 Pauling.....J.Am.C.S. 1933 55 1895

21 Kolthoff.....Rec. Trav. chim.1926 45 394

22 Bernal.....Proc. Lond. 1935 151 384

23 Percival & Ritchie.....J.C.S. 1936 1765

24 cf. Vermaas.....Rec. Trav. chim.1932 51 67

25 Böeseken & Vermaas.....J. Phys. Chem. 1931 35 1477

This is to certify that Mr HERBERT T. MACPHERSON successfully sustained an oral examination on the subject matter of his thesis by a committee of the Department. The examination was held in April of this year.

Members of
Committee.

4 May, 1937.